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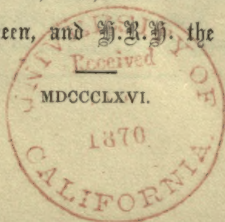LEOPOLD GMELIN.

VOL. XVII.

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## ORGANIC CHEMISTRY.
### VOL. XI.
ORGANIC COMPOUNDS CONTAINING FROM 34 TO 46 ATOMS OF CARBON.

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TRANSLATED BY

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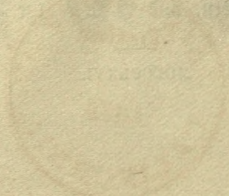
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## ERRATA.

Page 358, line 44, *for* $O^{16}$ *read* $O^{18}$.
,,    429,  ,,    4,  ,, alcohol ,, ether.
,,    499  ,,    5  ,, 22    ,, 23.

# APPENDIX TO 34-CARBON COMPOUNDS (*continued*).

THE roots of *Atropa Belladonna* yield a colouring matter which, according to Hübschmann, is identical with that of the berries. To obtain it, the roots are exhausted with alcohol of 90 p. c.; the tincture when distilled, leaves a residue of brownish-yellow acid syrup, together with resin. The latter is removed and the ˙syrup is mixed with ammonia and filtered, when there remains on the filter a small quantity of black granules, which are to be dissolved in acid, precipitated with ammonia, and washed with water and alcohol. The black powder thus obtained, Hübschmann's *Atrosin,* is insoluble in water, alcohol, and ether, but dissolves with fine red colour in dilute mineral acids, and in aqueous tartaric acid. (Hübschmann, *Schweiz. Pharm. Zeitschr; N. Jahrb. Pharm.* 19, 369.)

## 3. Leaf-red.

The *red colouring matter of autumn-reddened leaves,* the *Erythrophyll* of Berzelius is produced, according to Macaire-Princep, by the continued alteration of leaf-green which has first changed to leaf-yellow. Wittstein also regards it as a product of the action of sun-light on leaf-green, and terms it *Cissotannic acid* (xv, 516). — According to Schübler and Franck, autumn-reddened leaves contain leaf-yellow and a blue colouring matter which is reddened by acids; the experiments of Berzelius, however, contradict this. Chatin and Filhol (*Compt. rend.* 57, 39) seem to consider some kinds of leaf-red as identical with Fremy's cyanin (xvi. 522).

Leaf-red occurs in the leaves of plants which bear red fruit, especially in the leaves of *Sorbus aucuparia,* *Prunus Cerasus, Ribes rubrum,* and *Berberis vulgaris,* and is closely related to the red colour of the fruit (Berzelius). Autumn-reddened leaves occur, however, in plants which do not bear red fruit, the coloration having also no connection with the decay of the leaves (H. Mohl).

The red autumnal leaves of *Rhus Coriaria* and *Pyrus communis,* and the calyx of *Salvia splendens* yield, when treated with hot alcohol, a red resin which is turned green by alkalis and reddened again by acids, and is insoluble in oils (Macaire-Princep). — The brown autumnal leaves of the hornbeam are not turned green by caustic potash (Gmelin). A decoction of the leaves of *Vitis hederacea* is reddened by acetic acid, and gives with neutral acetate of lead a violet precipitate, which is turned green, but not dissolved, by caustic potash. When to the decoction an excess of neutral acetate of lead is added, the resulting precipitate is green; if, however, basic acetate of lead be gradually added, a violet precipitate is produced, which, after washing, is turned green by the neutral acetate (Legrip, *J. Chim. méd.* 23, 188) See xv, 516.

The leaf-red of Berzelius is obtained from the reddened leaves of

the cherry and of the currant. The leaves are exhausted with
alcohol; the alcohol is distilled off; and the remaining red liquid, after
filtering from resin and fat, is mixed with water, which produces no
cloudiness. Neutral acetate of lead is then added so long as the
resulting grass-green precipitate turns brown on standing. When the
colour no longer changes, the liquid is filtered and completely pre-
cipitated by neutral acetate of lead. The fine green precipitate is
washed on a filter, afterwards decomposed by hydrosulphuric acid, and
the solution is evaporated in a vacuum. Basic acetate of lead throws
down a little more leaf-red from the liquid previously precipitated by
the neutral acetate. — Leaf-red is darker, and more blood-red than
the colouring matter of the cherry, which it otherwise resembles. Its
solution, when evaporated, throws down a red-brown deposit, which
forms pale red-brown compounds with bases. Unchanged leaf-red
dissolves in water and alcohol, and forms, with bases, compounds
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of the fruit are green or blue. When the aqueous solution of leaf-
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and not blue, as would be the case if leaf-red were a blue colouring
matter reddened by acids (Berzelius, *Ann. Pharm.* 21, 265; *Pogg.*
42, 428).

Red cabbage contains a colouring matter, which is turned red by
acids and green by alkalis, and seems to be identical with that
of violets. Metallic salts and boracic acid colour the fresh liquid
green, and that reddened by acids blue (Murray). Carbonic and
other acids colour the green alkaline liquid blue (Bowen, *Schw.* 43,
382; Robinet and Guibourt), — Hydrosulphuric acid passed through
the liquid turns it green (Wolffgang, *Scher. N. Bl.* 1, 177); hydro-
sulphate of ammonia or protoxide of iron decolorises the liquid
which has been rendered green by alkalis (Kuhlmann, *Ann. Pharm.*
9, 286).

If the deposit thrown down from the expressed sap of the leaves
of *Antidesma alexiteria* be washed with cold water, warm ether after-
wards takes up therefrom a violet colouring matter, which is turned
green by alkalis and red by acids (Ridolfi, *Brugn. Giorn.* 17, 472).
The sap of *Mercurialis perennis* assumes in the air a blue colour, which
is reddened by acids (Runge). The sap of *Orobus niger* and *Polygonum
aviculare*, as well as the sap of *Boletus lactifluus*, turns blue only on
exposure to the air (Runge).

The nearly colourless sap expressed from the leaves of *Aloe
soccotrina*, when exposed to the air, even in the dark, gradually
assumes a red colour, passing at last to a splendid purple-violet.
Acids redden the sap and precipitate the colouring substance (Guyton-
Morveau. Fabroni, *Scher. J.* 2, 517 and 546).

The red colouring matter of the root-bark of *Lithospermum arvense*,
the red of Spanish pepper, chica-red, and nucin are treated of under
Alkanet-red (p. 17).

<div align="center">C. <i>Green Colouring Matters.</i></div>

## Leaf-green.

PROUST. *A. Gehl.* 1, 490.
VAUQUELIN. *Ann. Chim.* 83, 42.

JOHN. *Chem. Schriften*, 4, 161; 5, 26.
PELLETIER and CAVENTOU. *Ann. Chim. Phys.* 9, 194; *J. Pharm.* 3, 486; *N. Tr.* 3, 2, 313.
MACAIRE-PRINCEP. *Mem. de la Soc. de Phys. et d'hist natur. de Génève*, 4, 43; *N. Tr.* 18, 2, 226.
MARQUART. *Die Farben der Blüthen.* Bonn, 1835.
BERZELIUS. *Ann. Pharm.* 27, 296.
MULDER. *J. pr. Chem.* 33, 478.
VERDEIL. *Compt. rend.* 33, 689; *J. pr. Chem.* 55, 187.
L. PFAUNDLER. *Ann. Pharm.* 115, 37.
FRÉMY. *Compt. rend.* 50, 405; *N. J. Pharm.* 37, 211; *J. pr. Chem.* 87, 319.
LUDWIG and KROMAYER. *N. Br. Arch.* 106, 164.

*Resinous leaf-green.* Einhof's *Vegetable Wax*, Pelletier's *Chlorophyll*, Macaire-Princep's *Chromule verte.*

Various substances extracted by alcohol or ether from different plants, and coloured by leaf-green, were described by the older chemists as leaf-green. Berzelius, however, obtained the green colouring matter of leaves in a purer state. According to Frémy's investigations, even this leaf-green must be regarded as a mixture of a blue and a yellow colouring matter. The following views have also been put forward :—

*a.* Leaf-green bears a great resemblance to the colouring matter of the blood, and contains iron as an essential component (Verdeil). The root, seeds, and white parts of plants contain iron in the form of protoxide, which, when the parts become green, is converted into sesquioxide, and occurs as such in the reddened parts of plants; in leaf-green it occurs together with protoxide (E. Risler, *Kopp's Jahresb.* 1859, 560; extr. from *N. Arch. ph. nat.* 6, 206).

*b.* Leaf-green is a coloured substance, produced (probably by the influence of iron) from a colourless or faintly coloured compound, possibly quercetin, æsculetin, luteolin, or a decomposition-product of berberin, coloured by salts of iron (Hlasiwetz, *Ann. Pharm.* 112, 96; 115, 45). Pfaundler found that quercetin coloured by iron behaved differently from leaf-green obtained from grass. Hlasiwetz's view may, nevertheless, be correct in some cases.

*c.* According to Morot, leaf-green has the composition represented by the formula $C^{18}NH^{10}O^3$, and occurs, together with a fatty body, $C^6H^7O$, from which it is formed by the action of ammonia and carbonic acid. It is not capable of producing either blue or red vegetable colouring matters. His investigation, as well as that of Morren on chlorophyll and erythrophyll, is known to us only in the form of an extract (*Kopp's Jahresb.* 1859, 561) (Kr.).

Leaf-green is produced by the mixture of blue and yellow, and may be split up into these colours. When leaf-green, extracted by alcohol, is shaken with a mixture of two parts of ether and one part of slightly diluted hydrochloric acid, the ether takes up the yellow colour, whilst the hydrochloric acid beneath is coloured a splendid blue. If the two layers be mixed by the intervention of alcohol, the green colour is reproduced. The yellow colouring matter thus obtained is designated by Frémy, *Phylloxanthin;* the blue colour he terms *Phyllocyanin.* A less complete separation of the two is effected by adding to the alcoholic leaf-green hydrate of alumina, together with

small quantities of water, whereby, so long as the liquid is strongly alcoholic, a dark-green lake is precipitated, the alcohol remaining of a yellow colour. On treating this precipitate (or the yellowish-green lake formed by adding more water) with ether, alcohol, or oil of turpentine, the green colour is dissolved as a whole; bisulphide of carbon dissolves first the yellow, and leaves the undissolved portion of a dark-green colour. — Bases change leaf-green into yellow by the conversion of phyllocyanin into *phylloxanthin*. The latter substance is soluble in alcohol, and yields, with alumina, a yellow lake, from which alcohol, ether, and bisulphide of carbon extract the colouring matter. The alcoholic solution is turned green by hydrochloric acid; ether mixed with hydrochloric acid decomposes it into blue and yellow. The yellow colouring matter of young shoots and of etiolated leaves may also be split up, by means of ether and hydrochloric acid, into blue and yellow. It is coloured green by hydrochloric acid (Frémy).

When leaf-green is treated with hydrochloric acid, containing a trace of nitric acid, a nearly pure blue liquid is obtained (Filhol, *Compt. rend.* 50, 1182).

Phyllocyanin and phylloxanthin are obtained from the green colour of the young leaves of wheat in the following manner: The expressed sap mixed with alcohol is coagulated, and the coagulum, which retains the colouring matter, is washed and exhausted with ether. The ether is distilled off, and the residue first washed with cold, then dissolved in hot alcohol, and boiled for a few seconds with alcoholic potash, whereby the green colour is not altered. On dilution with water and addition of hydrochloric acid, a yellow precipitate, and a splendid blue liquid, copper-red by reflected light, are obtained. The latter, as the alcohol evaporates, deposits dark-blue flocks of phyllocyanin, which dry up to a dark-blue, brittle mass; or if the blue acid liquid be precipitated with basic acetate of lead, and the precipitate decomposed with hydrosulphuric acid, the colouring matter goes down with the sulphide of lead. The precipitate is then to be washed with ether to remove the yellow, and exhausted with alcohol containing hydrochloric acid; on evaporating the solution, dark-blue phyllocyanin remains. Nitric acid turns it green, then orange-yellow; hydrochloric acid colours the alcoholic solution a splendid blue-green. When heated in a glass tube, it yields a violet distillate. Contains, at 100°, 50·96 p. c. C, 8·52 H, 7·01 N, and 33·51 O, corresponding to the formula $C^{34}N^2H^{24}O^{17}$ (Ludwig & Kromayer). — The yellow precipitate thrown down by hydrochloric acid forms, after washing with alcohol, a yellow, viscous mass. It is not altered by digestion with caustic soda. After removing the soda, it forms with water a yellow emulsion, the colouring matter of which is taken up by ether and hydrochloric acid when shaken therewith. The ethereal solution, when evaporated, leaves a residue. which is dissolved (excepting wax) by bisulphide of carbon, and left on evaporation in the form of a tough, yellow mass. It is coloured green by nitric acid (Ludwig & Kromayer).

¶. According to Stokes (Proc. Roy. Soc. xiii, 144), the leaf-green of land-plants is a mixture of four substances, two green and two yellow, all possessing highly distinctive optical properties. The green substances yield solutions exhibiting a strong red fluorescence; the yellow substances do not. These four substances are soluble in the same solvents, and three of them are very easily decomposed by acids,

or even by acid salts, such as binoxolate of potash. Frémy's phillo-cyanin is mainly the product of decomposition by acids of one of the green bodies; his philloxanthin differs in composition and properties according to the mode of preparation. Green sea-weeds agree with land-plants, except as to the relative proportion of the colouring substances present; but in olive-coloured sea-weeds (*Melanospermeæ*) the second green sub-stance is replaced by a third green substance, and the first yellow substance by a third yellow substance, to the presence of which the dull colour of these plants is due. The red colouring matter of the red sea-weeds (*Rhodospermeæ*) which the plants contain in addition to chloro-phyll appears to be an albuminous substance. (See also *Chem. Soc. J.* xvii, 309, 314. ¶)

*Older investigations. By Berzelius.* — Leaf-green is a peculiar sub-stance, which is not decomposed by acids and alkalis, but forms definite compounds therewith. Like other colouring principles, it is destroyed by light, air, and chlorine. It may be obtained in three modifications.

α. *Leaf-green having the colour of fresh leaves.* The fresh leaves of *Crataegus Aria*, collected in August, are bruised and exhausted with ether; the dark-green tincture is distilled over a water-bath till nearly the whole of the ether is removed; the solution is separated from the deposit thereby produced; and the latter is washed with alcohol so long as it imparts a dark-green colour thereto. The alcoholic tincture contains leaf-green of the first modification, whilst the separated ethe-real solution, and the portion of the deposit insoluble in alcohol, con-tain leaf-green of the second modification. The alcoholic solution is evaporated to dryness, and the residue treated with strong hydro-chloric acid, which leaves a little dark substance (β). Water is added to the dark-green filtrate so long as precipitation ensues, and the precipitate is washed in succession with cold and hot water, the latter being coloured yellow. The leaf-green thus obtained and dried, has already undergone change, since it dissolves only with difficulty in alcohol and ether, with black-green colour. It is, therefore, digested for twelve hours in a weak solution of caustic potash, afterwards diluted with twice the volume of water, and heated to the boiling-point. The splendid grass-green liquid is filtered from the black powder deposited, and slightly supersaturated with acetic acid, when the leaf-green is thrown down in fine green flakes, which are collected, washed, and dried.

Dark-green, earthy mass, easily triturable to a grass-green powder. When heated to 200°, it does not fuse, and gives off merely a trace of moisture. On treating this heated leaf-green with hydrochloric acid, or caustic potash, a small quantity of black powder remains undis-solved; the greater part, however, is still undecomposed. — Leaf-green, submitted to dry distillation, melts, puffs up, and gives off first a trace of moisture, then a colourless oil, together with a red non-crystalline sublimate; at last a dark oil passes over, whilst a perfectly combustible charcoal remains behind. The red sublimate dissolves in water, hydrochloric acid, alcohol, and ether. It is not saponified by caustic potash, and carbonises when heated, without again subliming. Leaf-green is decolorised and converted into a fatty mass by a mix-ture of hydrochloric acid and chlorate of potash. Nitric acid decom-poses it. Hot oil of vitriol turns it brown, and evolves sulphurous

acid. An alcoholic tincture of fresh leaves is bleached in a few hours in sunshine. In one experiment leaf-yellow (xvi., 515) seemed to be produced.

Leaf-green is insoluble in water, even when boiling. Cold oil of vitriol dissolves it with magnificent green colour; the solution is permanent except when heated: it is precipitated by water. Hydrochloric acid of sp. gr. 1·14 dissolves it with deep emerald-green colour, generally leaving behind a small quantity of pale-yellow fatty substance: the solution is partially precipitated by water, and completely precipitated by neutralisation with carbonate of lime; it leaves the leaf-green as a dark-green pellicle when evaporated. — Moist leaf-green dissolves in ammonia and carbonate of ammonia, and in caustic potash and soda, with fine green colour, and is precipitated from the solutions by acetic acid in large flocks, which appear emerald-green by transmitted light. Dried leaf-green leaves a dark residue when dissolved in caustic potash. The solution in ammonia and in the carbonates of the alkalis has a dingy colour. The ammoniacal solution loses its ammonia when evaporated; the solution in caustic potash or its carbonate deposits, when concentrated, a potash-compound of leaf-green soluble in water, but insoluble in alcohol. — Lime- and baryta-water precipitate ammoniacal leaf-green with pale-green colour. Alkaline leaf-green precipitates solution of alum, with splendid green colour; the alcoholic solution precipitates neutral acetate of lead with grass-green colour.

Leaf-green dissolves slightly in cold, more freely in boiling acetic acid, and is precipitated from the solution by water. It dissolves in alcohol with grass-green colour (the dried substance slowly with blue-green colour), and is again thrown down by water. Soluble in ether, oil of turpentine, and fixed oils (Berzelius).

β. *Leaf-green having the colour of dried leaves.* — Obtained from fresh leaves in the preparation of α. The ethereal solution, obtained as described, is added to the deposit insoluble in alcohol, and evaporated; and the residue is again dissolved in ether and mixed with fuming hydrochloric acid, which is coloured an opaque green. So much ether is then added that it is not completely taken up by the hydrochloric acid, and, after shaking and standing for 24 hours, the deep-yellow solution is decanted, the remaining ethereal solution being rinsed out with a little ether. The solution is warmed to drive off the ether held in solution, and filtered; the fat remaining on the filter is washed with hydrochloric acid; and the acid solution is mixed with water as long as a precipitate is produced, then filtered, and saturated with marble, whereby the leaf-green is thrown down. The precipitate produced by water is treated with hydrochloric acid, which leaves leaf-green of the third modification behind; and the filtrate (now no longer precipitated by water, since it contains only β) is to be precipitated by marble as before.

β leaf-green is of a dirty yellowish dark-green colour, like dry, long-kept leaves. It is not precipitated from its solution in hydrochloric acid by water, except in presence of α or γ. It behaves in the same manner as α with chlorine and nitric acid, and generally also with solvents and precipitants; the solutions and precipitates, however, exhibit other colours. The solution in dilute hydrochloric acid is decolorised by zinc. The solutions in acetic acid, alcohol, and ether are grey-green in thin films and reddish-blue in thicker layers (Berzelius).

γ. *Third modification of leaf-green.* — Obtained in the preparation of β, as a black residue, insoluble in hydrochloric acid of sp. gr. 1·14. It is purified by washing with water, drying, dissolving in boiling alcohol (which is effected with difficulty), and evaporating the dark-green solution over the water-bath. — It forms a shining residue, nearly black by daylight, dark-green by artificial light. Hard, and easily reduced to a dark-green power. Attracts moisture readily from the air and becomes pasty. Dissolves very slightly in hydrochloric acid with yellow colour, and is not thrown down again by water. Insoluble in cold, slightly soluble in boiling acetic acid, forming a fine green solution, from which it is deposited of a green colour on cooling. Difficultly soluble in alcohol, and very slightly soluble in ether (Berzelius).

Leaf-green prepared from poplar leaves, according to the directions of Berzelius, contains, at 102°, 54·74 p. c. C., 4·82 H., 6·68 N., and 33·76 O. (Mulder).

The dark blue-green solution of leaf-green in oil of vitriol, when covered with a layer of alcohol, assumes a dark indigo-blue colour, which is imparted to the alcohol (Marquart).

Verdeil obtains his (ferruginous) leaf-green by exhausting leaves with boiling alcohol, and mixing the tincture with hydrate of lime, whereby the fatty bodies are retained in solution, and the leaf-green is precipitated. The lime precipitate is treated with hydrochloric acid and ether, which take up the leaf-green and leave it behind on evaporation.

When grass is expressed with water, the liquid heated to boiling, and the albuminous leaf-green which separates exhausted with alcohol, the tincture leaves on distillation a soft dark-green jelly. This is agitated with boiling water; the liquid is decanted; the residue dissolved in warm hydrochloric acid; and the solution, after cooling, filtered and precipitated with hot water. The flocks thus precipitated, form, when dried and triturated, a dark-blue powder, containing on the average (after deducting 0·92 p. c. ash containing iron) 60·84 p. c. carbon, 6·38 hydrogen, 32·78 oxygen, and an unimportant trace of nitrogen (0·037 p. c.). When boiled with caustic potash, it does not yield the decomposition-products of quercetin (Pfaundler).

*Euchema spinosum* Ag., a sea-weed from the East Indian Archipelago, contains a variety of leaf-green which is soluble in alcohol and ether, and insoluble in hydrochloric acid (Oudemanns, *N. Br. Arch.* 87, 292). The leaf-green of *Cetraria islandica*, the tallochlor of Schnedermann and Knop, behaves in a similar manner. (See under Cetraric acid, $C^{36}H^{16}O^{16}$, p. 22). — A green colouring matter from infusoria, which, according to M. Schultz (*Compt. rend.* 34, 683) agrees with leaf-green, but, according so Salm-Horstmar (*Pogg.* 94, 466) differs therefrom, will be described in another place.

The two following green colouring matters differ from leaf-green.

*Green colouring matter of Thistle-tops, Artichokes, and undeveloped Flower-buds.* — When these parts of plants, while still white, are boiled with water or pressed, colourless liquids, unchangeable in the air, are obtained, which turn green in the air on addition of a little soda or lime-water, and in presence of excess of alkali assume a yellow colour. From these green solutions, alum, neutral acetate of lead, and stannic oxide throw down fine dark-green lakes, which are not altered by drying.

On decomposing the lead-precipitate with alcohol containing sulphuric acid, and mixing the brown yellow tincture with a large quan-

tity of ether, the colouring matter is precipitated. When collected, washed with water, and dried, it is yellowish-brown, infusible and non-volatile, and contains nitrogen and traces of ash. — The green colour is insoluble in water, but soluble in oil of vitriol with fine red colour; it is not affected by hydrochloric or acetic acid. The easily formed solution in caustic alkalis and their carbonates is of a fine green colour, and is precipitated by acids. It is decolorised by liquids in a state of fermentation, and regains its colour on exposure to the air. — The colour is slightly soluble in *alcohol*. It dyes prepared cotton-wool (Verdeil, *Compt. rend.* 47, 442 ; *J. pr. Chem.* 77, 461).

*Colouring matter of Monotropa Hypopitys.* — Appears to be formed by the action of the air on some colourless substance contained in the plant, the cut surfaces of the plant assuming a violet colour only on exposure.

An aqueous decoction of the fresh plant deposits, on standing, a dark blue-green powder consisting of microscopic, round, black granules. — The same powder is obtained by digesting the plant, without access of air, in alcohol previously freed from air by boiling, and distilling the tincture to remove the greater part of the alcohol, when a small quantity of black granules is deposited. — This substance appears to contain nitrogen. — When *heated* it evolves an odour of cloves, then gives off vapours having the smell of tobacco, together with oily drops, and leaves charcoal. — It dissolves gradually in boiling *water* with brown colour : the solution has an acid reaction, and is precipitated green by acetate of iron, dirty-yellow by mercurous nitrate, and yellow by neutral acetate of lead ; tincture of iodine colours it a transient cherry-red. — It dissolves in *oil of vitriol* without assuming a dark colour, and is thrown down from the solution by water. *Hydrochloric acid* dissolves it with emerald-green colour ; the solution is not precipitated by water. Cold *nitric acid* dissolves it with greenish colour. — It dissolves easily in aqueous *ammonia* and *alkalis* with black colour, and is precipitated from the solutions by acids in cherry-red flocks. — Insoluble in *alcohol* and *ether* (Reinsch, *Jahrb. pr. Pharm.* 25, 193).

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# COMPOUNDS CONTAINING 36 ATOMS OF CARBON.

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*Primary Nucleus* $C^{36}H^{18}$.

## Retene.

$C^{36}H^{18}$.

B. TROMMSDORFF. *Ann. Pharm.* 21, 126.

E. KRAUS. *Pogg.* 43, 141 ; *Ann. Pharm.* 28, 345.

STEENSTRUP (and FORCHHAMMER). *Ann. Pharm.* 41, 39 ; *J. pr. Chem.* 20, 459.

KNAUSS. *Ann. Pharm.* 106, 391 ; *J. pr. Chem.* 82, 334.

FEHLING. *Ann. Pharm.* 106, 388 ; abstr. *J. pr. Chem.* 74, 507 ; *Chem. Centr.* 1858, 543 ; *Kopp's Jahresber*, 1858, 439.

FRITZSCHE. *Petersb. Acad. Bull.* 17, 68 ; *J. pr. Chem.* 75, 281 ; abstr. *Ann. Pharm.* 109, 250 ; *Compt. rend.* 47, 723 ; *Rép. Chim. pure* 1, 264 ; *Kopp's Jahresb.* 1858, 440. — *N. Petersb. Acad. Bull.* 3, 88 ; *J. pr. Chem.* 82, 321 ; abstr. *Chem. Centr.* 1861, 197 ; *Kopp's Jahresb.* 1860, 475.

Discovered by Fikentscher (*Bericht über die Vers. deutscher Naturf. zu Prag*, 1837) and Trommsdorff : described by Kraus as *Scheererit*, and by Steenstrup as *Phylloretin*. A hydrocarbon obtained by Knauss, as a product of the distillation of resin, was recognised by Fritzsche as identical with the above substances. Principally investigated by Fritzsche.

*Occurrence.* In fossil pine-trunks, in deposits of peat and lignite ; in a peat-bed on the Fichtelberg (Fikentscher, Trommsdorff) ; in a lignite deposit near Utznach, Canton St. Gall (Könlein, Kraus) ; in Danish peat-bogs (Steenstrup). It forms a thin covering of small, fatty, shining scales, soft to the touch, and is also diffused through the wood. On the Fichtelberg and near Utznach it is found associated with Fichtelite. — A resin, melting at 108°, obtained by Herz (*N. Repert.* 10, 506) in very small quantity from the lignite of the Hohenpeissenberg in Southern Bavaria, may possibly be retene.

*Formation.* In the dry distillation of pine-wood rich in resin, it passes over with the tarry liquors, and separates therefrom in scales having the appearance of paraffin (Knauss). By submitting colophony to dry distillation and passing the vapour through a red-hot tube, Fritzsche obtained several hydrocarbons forming compounds with picric acid, amongst them probably retene : metanapthalin, which is obtained in a similar manner, is perhaps impure retene (Fritzsche).

*Preparation. From Fossil Wood.* The comminuted wood is exhausted by boiling with alcohol ; the greater part of the alcohol is then distilled off ; and the remainder of the decoction is evaporated to dryness and treated with sulphide of carbon, which dissolves retene and other substances, leaving a red-brown acid resin. The sulphide of carbon is removed by distillation, and the residue dissolved, together with picric acid, in benzene, when, on cooling, a compound of retene with picric acid and benzene separates out in yellow needles. These are pressed and recrystallised from alcohol, with addition of excess of picric acid, and the compound of retene and picric acid is decomposed in a manner similar to that described at page 165, vol xvi : the separated retene is recrystallised from alcohol (Fritzsche). Kraus boils the wood in alcohol and purifies the retene which separates by recrystallisation. When the crystals obtained from the wood-remains in Danish peat-bogs are dissolved in boiling alcohol, tekoretin crystallises out first, and afterwards retene (Steenstrup).

*Properties.* Soft, shining laminæ, resembling boracic acid, unctuous to the touch (Trommsdorff). Nacreous, less loose than napthalin (Fehling). Melts at 87·5° (Steenstrup), at 98—99° (Fehling), at 107·5° (Trommsdorff), at 114° (Kraus). Fused retene solidifies at 90°, the temperature rising to 95° (Fritzsche). Solidifies, on cooling, to a white, very brittle mass. Evaporates gradually in the air and over the water-bath ; on melting it gives off white clouds, which condense to a woolly sublimate (Kraus). Volatilises slightly with water-vapour. Boils at a temperature about the boiling point of mercury, and distils almost unchanged, the distillate becoming brown and the residue

carbonising only towards the end of the distillation (Fritzsche, Fehling). See below. — Inodorous, tasteless. Sp. gr. after fusing and solidifying, 0·88 (Trommsdorff): according to Fehling, it sinks in cold, but floats on boiling water.

| | | H. Trommsdorff. | Kraus. | Steenstrup. | Fehling. mean. | Fritzsche. mean. | |
|---|---|---|---|---|---|---|---|
| | | | | | | earlier. | later. |
| 36 C .... | 216 .... | 92·31 .... | 90·91 .... | 91·36 .... | 90·18 ... | 91·68 .... | 92·19 .... 92·41 |
| 18 H ... | 18 .... | 7·69 .... | 7·56 .... | 7·42 .... | 9·24 .... | 8·36 .... | 7·60 .... 7·78 |
| C³⁶H¹⁸... | 234 .... | 100·00 .... | 98·47 .... | 98·78 .... | 99·12 ... | 100·04 .... | 99·79 ....100·19 |

Polymeric with benzene (Trommsdorff, Kraus).

*Decompositions.* 1. Fused retene gives off, at 160°, a number of small bubbles, boils at 200°, turning brown, and yields first a colourless (but altered), then a brown distillate, and at last a black tar, charcoal being left behind. The distillate melts with the warmth of the hand, and does not afterwards solidify when left at rest, but if shaken, it partially solidifies in laminæ. By repeated distillation it is obtained quite fluid, and no longer yields retene when dissolved in alcohol. The crystals of the distillate, freed from retene, contain 85·91 p. c. C., 10·84 H.; the oil contains 86·18 p. c. C., and 11·2 H., the two are therefore isomeric (Kraus). This retene probably contained fichtelite (Kr.). See above. — 2. Retene *burns* with a bright smoky flame (Trommsdorff, Kraus). — 3. *Nitric acid* converts retene into a resin (Fritzsche); more dilute acid also forms crystalline products (Fehling). Trommsdorff's retene is not attacked by fuming nitric acid; that of Kraus is dissolved, and is thrown down from the solution by water white and crystalline. — 4. Retene forms coloured resins by treatment with *chromic acid* (Fehling), and with *hydrochloric acid and chlorate of potash* (Fritzsche). — 5. By prolonged contact with *oil of vitriol*, retene is dissolved, evolving an odour of sulphurous acid, and forms retene-bisulpholic acid, which crystallises out in combination with sulphuric acid on standing. Retene heated with oil of vitriol yields sulpho-retene (Fritzsche).

Knauss added retene to a mixture of fuming and ordinary oil of vitriol, warmed the mixture to promote solution, and saturated the liquid, after dilution, with carbonate of lead. In this way he obtained, on one occasion, a lead-salt, which solidified to a jelly on cooling the concentrated solution, and contained, after pressing and drying at 100°, 26·92 p. c. C., 2·30 H., and 42·82 PbO. Another time, on supersaturating oil of vitriol with retene and diluting the solution, unchanged retene separated, together with a white powder; the liquid when saturated with carbonate of lead, yielded, besides the above salt, retene-bisulpholate of lead, and white flocks of a third lead-salt, soluble only in boiling water, and containing 46·80 p. c. C., 4·47 H., and 29·82 PbO.

6. Retene is not acted upon by *potassium* (Trommsdorff, Steenstrup), or by *caustic potash*, or *lime* (Fehling), even when distilled therewith.

Retene is insoluble in *water*. — It dissolves with difficulty in cold, and much more readily in boiling, *alcohol*. One part of retene dissolves in 28·6 pts. of boiling alcohol of 94 p. c. (Trommsdorff), in 40 pts. of 75 p. c.; on cooling 1/800th remains in solution (Fritzsche). — Easily soluble in warm *ether*, and in *volatile* and *fixed oils*.

*Retene with Picric acid.* Retene is dissolved together with three parts of picric acid in hot alcohol or ether, and the crystals are collected and pressed. — Woolly, delicate, orange-yellow needles, darker after fusion. Melts, when heated, to an orange-red liquid, which solidifies at 125°. — Washing with alcohol decomposes it; alcohol of

75 p. c. dissolves picric acid and leaves retene behind ; alcohol of 90 p. c. dissolves a portion of the compound as a whole, and in the remainder crystals of retene are deposited (Fritzsche).

| | | | | Fritzsche. earlier. | | mean. later. |
|---|---|---|---|---|---|---|
| 48 C | ..................... | 288 | .... | 62·20 .... 62·67 | ........ | 62·40 |
| 3 N | ..................... | 42 | .... | 9·07 .... | | |
| 21 H | ..................... | 21 | .... | 4·54 .... 4·55 | ........ | 4·73 |
| 14 O | ..................... | 112 | .... | 24·19 .... | | |
| $C^{36}H^{18},C^{12}H^3X^3O^2$ | .... | 463 | .... | 100·00 | | |

Contains 51·38 p. c. retene and 48·62 p. c. picric acid (Fritzsche). (Calc. 50·54 p. c. retene, 49·46 picric acid).

*Retene with Picric acid and Benzene.* — When a mixture of retene and picric acid is dissolved in benzene, there separate on cooling needles containing 13·90 to 14·47 p. c. benzene ; they become opaque in the air, and lose the whole of the benzene (Fritzsche).

| | | | | | Fritzsche. |
|---|---|---|---|---|---|
| $C^{36}H^{18}$ | ..................... | 234 | ........ | 43·25 ........ | 43·75 |
| $C^{12}H^6$ | ..................... | 78 | ........ | 14·42 ........ | 14·47 |
| $C^{12}H^3X^3O^2$ | ..................... | 229 | ........ | 42·33 ........ | 42·35 |
| $C^{36}H^{18},C^{12}H^6,C^{12}H^3X^3O^2$ | .... | 541 | ........ | 100·00 ........ | 100·57 |

*Conjugated Compounds of Retene.*

## Sulphoretene.

$$C^{36}H^{20}S^2O^8 \;=\; C^{36}H^{18},2SO^3,2HO.$$
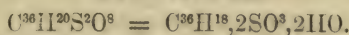
On diluting the solution of retene in oil of vitriol with an equal volume of water, filtering the liquid from the crystals of a hydrated compound of retene-bisulpholic acid and sulphuric acid which form on cooling, and boiling the mother-liquor with more retene, Fritzsche found that the retene floated unattacked on the surface of the liquid ; he therefore added gradually twice the volume of oil of vitriol and heated the mixture to 170° or 180°, till the retene disappeared. The black-green liquid, after cooling, was decanted from the tar simultaneously produced, diluted with water, filtered, and neutralised with ammonia, whereby sulphoretene was precipitated. The precipitate was washed, dried, freed from admixed retene by treatment with ether, and crystallised from boiling water or alcohol.

*Properties.* Deposited from water in thin laminæ, and from alcohol as a light sandy powder or in crusts. Melts only at the point of decomposition.

| | | | | | Fritzsche. |
|---|---|---|---|---|---|
| 36 C | ..................... | 216 | ........ | 65·03 ........ | 65·23 |
| 20 H | ..................... | 20 | ........ | 6·02 ........ | 6·08 |
| 2 S | ..................... | 32 | ........ | 9·67 ........ | 9·74 |
| 8 O | ..................... | 64 | ........ | 19·28 ........ | 18·95 |
| $C^{36}H^{18},S^2H^2O^8$ | .... | 332 | ........ | 100·00 ........ | 100·00 |

*Decompositions.* When *heated* it blackens and yields a solid distillate which is easily soluble in ether and combines with picric acid, like retene. On digestion with *oil of vitriol*, it reddens, turns semi-fluid, and dissolves with red colour. Water, gradually taken up by the solution, precipitates flocks ; added in larger quantity, it forms a clear solution which deposits a large quantity of needles on cooling. The solution is no longer precipitated by ammonia, but forms therewith difficultly soluble granules, probably of retene-bisulpholate of ammonia.

*Combinations.* Sulphoretene is wetted with difficulty by cold *water* and dissolves but slightly. Boiling water dissolves it abundantly but slowly.

Dissolves abundantly in hot dilute *mineral acids*, and is deposited from the solution, on cooling, in flocks or in the form of a jelly, or, when ammonia is added to the hot solution, in laminæ.

*With Hydrochloric acid.* — Obtained by boiling sulphoretene with concentrated hydrochloric acid. It is deposited from the hot liquid as a heavy oil, forming, on cooling, a crystalline solid which is immediately decomposed by water.

*With Oxalic acid.* — When aqueous oxalic acid is boiled with an excess of sulphoretene, the filtrate first deposits unchanged retene, and, on further cooling and standing, a white granulated powder, which seems not to be decomposed by water.

*With Picric acid.* — The solution of sulphoretene in hot aqueous picric acid solidifies, on cooling, to a jelly, which dries up to a dark orange-yellow, paper-like mass, and crystallises from alcohol in yellow needles very difficultly soluble in benzene.

Sulphoretene dissolves freely in boiling aqueous *ammonia*, crystallising therefrom on cooling. It dissolves slightly in solution of *caustic potash.*

Soluble in cold, and much more freely in boiling *alcohol.* Nearly insoluble in *bisulphide of carbon*, *ether*, and *benzene.*

## Retene-bisulpholic Acid.

$$C^{36}H^{18}S^4O^{12} = C^{36}H^{18},4SO^3.$$
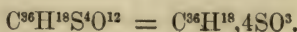
FRITZSCHE. *J. pr. Chem.* 82, 330.
KNAUSS. *J. pr. Chem.* 82, 334.

*Retendisulfosäure. Disulforetensäure* (see p. 10).

*Preparation.* Retene is added to oil of vitriol slightly diluted with water, and the solution is allowed to stand till it crystallises in a solid mass ; it is then diluted with water, neutralised with baryta and carbonate of baryta, filtered from the precipitated sulphate, and concentrated to crystallisation. The retene-bisulpholic acid is liberated from the baryta-salt by sulphuric acid (Fritzsche).

The aqueous solution, when evaporated, yields a syrup which solidifies, on cooling, to a tough, waxy mass of confused needles. The alcoholic solution yields larger needles (Fritzsche).

When subjected to *dry distillation* it puffs up, evolves sulphurous acid, and yields a distillate which solidifies on cooling, and resembles the baryta-salt (Fritzsche).

The acid dissolves in *water*. The solution of retene in oil of vitriol deposits, on absorption of water, oily drops which dissolve in a larger quantity of water (Fritzsche).

A solution of retene in moderately dilute oil of vitriol forms, on standing, crystals of a compound of *retene-bisulpholic acid with sulphuric acid*, which convert the saturated solution into a pulpy mass. From 100 parts of retene, 280 parts of these crystals (containing 58·13 p. c. free sulphuric acid) are obtained. They may therefore be regarded as a compound of 1 at. of retene-bisulpholic acid with 10 at. of oil of vitriol. They dissolve easily in water, and are apparently deposited therefrom in hydrated crystals (Fritzsche).

*Retene-bisulpholate of Baryta.* — Preparation, above. Delicate, colourless needles, giving off 14·46 p. c. water at 175° (10 at. = 14·53 p. c. HO), and absorbing it again on exposure to moist air. — Submitted to dry distillation it yields a liquid distillate, which solidifies on cooling, and combines with picric acid to form yellow needles (Fritzsche).

| | | Dried. | | Fritzsche. |
|---|---|---|---|---|
| 36 C | 216 | ........ | 40·81 | ........ | 40·78 |
| 16 H | 16 | ........ | 3·02 | ........ | 3·07 |
| 2 Ba | 137 | ........ | 25·90 | ........ | 25·85 |
| 4 S | 64 | ........ | 12·14 | ........ | 12·16 |
| 12 O | 96 | ........ | 18·13 | ........ | 18·14 |
| $C^{36}H^{16}Ba^2,4SO^3$ | 529 | ........ | 100·00 | ........ | 100·00 |

*Retene-bisulpholate of Lead.* — See p. 10. Dissolves slightly in cold, and freely in boiling water, separating therefrom on cooling in white flocks (Knauss).

| | | | | Knauss. |
|---|---|---|---|---|
| 36 C | 216 | ........ | 36·00 | ........ | 35·93 |
| 16 H | 16 | ........ | 2·67 | ........ | 3·17 |
| 4 S | 64 | ........ | 10·67 | | |
| 10 O | 80 | ........ | 13·33 | | |
| 2 PbO | 224 | ........ | 37·33 | ........ | 37·43 |
| $C^{36}H^{16}Pb^2,4SO^3$ | 600 | ........ | 100·00 | | |

The acid dissolves easily in *alcohol* (Fritzsche).

Primary Nucleus $C^{36}H^{24}$.

# Helenene.

$C^{36}H^{24}$ ?

GERHARDT. *Ann. Chim. Phys.* 72, 181. — *N. Ann. Chim. Phys.* 12, 190.

When helenin is distilled with anhydrous phosphoric acid, a light oil passes over, with evolution of carbonic oxide, and a black viscous

residue remains behind. The distillate is treated repeatedly with fuming sulphuric acid to remove unchanged helenin, precipitated with water, dried, and rectified.

*Properties.* Yellow or colourless oil, lighter than water. Boils at 285° to 295° (*Traité*, 4, 298). Odour faint, resembling that of acetone.

|  |  |  |  |  | Gerhardt. mean. |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| 36 C | ........ | 216 | ........ | 90 | ........ | 89·33 | 38 C | ........ 228 | ........ | 89·76 |
| 24 H | ........ | 24 | ........ | 10 | ........ | 10·22 | 26 H | ........ 26 | ........ | 10·24 |
| C³⁶H²⁴ | ...... | 240 | ........ | 100 | ........ | 99·55 | C³⁸H²⁶ | ...... 254 | ........ | 100·00 |

Gerhardt hesitates between these two formulæ.

Helenene *burns* with a smoky flame. — In *nitric acid* it turns red, then green, and is precipitated by water apparently unaltered; when heated it is converted into a resin. Cold fuming *oil of vitriol* is without action on helenene; the hot liquid carbonises it: if the mixture be gently heated, the whole dissolves completely with brown-red colour, and on diluting the solution with water, neutralising with carbonate of baryta, and evaporating the filtrate, *helenene-sulphate of baryta* (containing, at 100°, 5·9 p. c H., and 17·75 BaO) is obtained. The salt is bitter, easily soluble in water, and non-crystalline.


## Carotin.

$$C^{33}H^{24}O^2 = C^{36}H^{24},O^2 ?$$
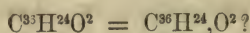
Wackenroder. *Mag. Pharm.* 33, 148; abstr. *Berzel. Jahresber.* 12, 277.
Zeise. *J. pr. Chem.* 40, 297; *Ann. Pharm.* 62, 380.
Aug. Husemann. *Dissert. über Carotin und Hydrocarotin*, Gött. 1860; *Ann. Pharm.* 117, 200; abstr. *Chem. Centr.* 1861, 343; *Rép. Chim. pure* 3, 407; *Kopp's Jahresb.* 1861, 754.

Discovered by Wackenroder in 1832, Vauquelin (*Ann. Chim. Phys.* 41, 48) having previously described a resinous red-yellow colouring matter obtained from carrots. Especially investigated by Husemann.

*Occurrence.* In the roots of the cultivated *Daucus Carota.*

*Preparation.* Rasped carrots are subjected to pressure, and the press-cake is repeatedly agitated with water and again pressed; the united liquids are precipitated by dilute sulphuric acid, with addition of a little tincture of galls, and the precipitate of carotin, hydrocarotin, and other substances (principally vegetable albumin) is pressed and boiled, in its half-dry state, six or seven times with 5 or 6 times its volume of alcohol of 80 p. c., which takes up hydrocarotin and mannite. It is then dried and exhausted by boiling six or eight times in bisulphide of carbon; the greater part of the bisulphide is distilled off; and the residue is mixed with an equal volume of alcohol and left at rest, when the carotin crystallises. It is washed with

boiling alcohol of 80 p. c., and at last with boiling absolute alcohol till the washings have only a slight yellow colour (Husemann). Zeise boils the precipitate produced by sulphuric acid in diluted carrot-juice, after washing, with concentrated solution of caustic potash, and washes it with dilute sulphuric acid and with weak and strong alcohol, in succession, to dissolve fat, vegetable albumin, and other substances : the carotin remaining behind is crystallised from bisulphide of carbon with the help of absolute alcohol. — Wackenroder obtains carotin by exhausting with ether either the sliced roots washed and dried, or the coagulum formed by heating the expressed juice. The residue left on evaporating the ethereal solution is shaken either with cold strong alcohol, or repeatedly with ammonia, to remove fatty matter ; it is then again dissolved in ether, and, after addition of alcohol, left to crystallise.

*Properties.* Carotin forms red cubes, or octahedral crystals, sometimes exhibiting a golden or satiny lustre. At $100°$ it assumes a splendid red colour, resembling that of copper reduced by hydrogen (Husemann, Zeise). Melts at $168°$ (Zeise), $167.8°$ (Husemann), to a thick dark-red liquid, which solidifies in an amorphous condition on cooling. See below. Inodorous, tasteless, neutral (Wackenroder); according to Zeise, the odour is faint and agreeable ; according to Husemann, powerful, especially on warming, like that of orris root. Heavier than water.

|  |  |  |  |  | Husemann. mean. |
|---|---|---|---|---|---|
| 36 C | ............ | 216 | ........ | 84·37 | ........ 84·06 |
| 24 H | ............ | 24 | ........ | 9·37 | ........ 9·78 |
| 2 O | ............ | 16 | ........ | 6·26 | ........ 6·16 |
| $C^{36}H^{24}O^2$ | ............ | 256 | ........ | 100·00 | ........ 100·00 |

Zeise proposed the formula $C^5H^4$.

*Decompositions.* 1. In diffused *light*, and more quickly in sunshine, it becomes paler and colourless from without inwards, so that on exposure for three weeks the red colour disappears completely. The resulting colourless product is difficultly soluble in bisulphide of carbon and benzene, easily soluble in alcohol and ether, and non-crystallisable ; it turns red again when heated (Husemann). This change, supposed by Wackenroder to be caused by an admixture of fat turning rancid, is suffered also by pure carotin (Husemann). — 2. Carotin dried at $90°$, when subjected to a gradually increasing temperature, loses at $150°$, 16 p. c. in weight, and becomes inodorous and discoloured : when thus altered, or when fused, it behaves towards solvents in the same manner as bleached carotin (Husemann, Zeise). Carotin, heated above its melting-point, forms a limpid liquid ; after being heated to $250°$ it is soft and yellowish-red on cooling ; at a higher temperature ($287°$, Zeise) it carbonises, with empyreumatic odour, giving off a little gas and a colourless oil (Husemann, Zeise). — 3. When heated in the *air*, carotin takes fire and *burns* without leaving a residue (Zeise).

4. Dry *chlorine* converts carotin into quadrichlorcarotin. Bromine and iodine also form substitution-products (Husemann). — 5. Carotin dissolves in cold *fuming nitric acid* with yellow-red colour, and is precipitated by water as lemon-yellow nitrocarotin, which is insoluble in bisulphide of

carbon, and difficultly soluble in ether and absolute alcohol. — 6. *Oil of vitriol* dissolves carotin, forming a fine purple-blue solution, from which water precipitates amorphous carotin in dark-green flocks. Carotin which has been altered by heat or exposure to air dissolves in oil of vitriol with brown colour. — 7. Dry *sulphurous acid* colours carotin deep indigo-blue without producing further change. Blue carotin turns red again at 125°, or when warmed with caustic potash; it does not contain sulphurous acid. Aqueous sulphurous acid slowly colours carotin coffee-brown; caustic potash restores the red colour. — 8. Carotin is rendered uncrystallisable by boiling with alcoholic *potash*. — It is not decomposed by nascent hydrogen, nor by hydrosulphuric acid, alcoholic hydrosulphate of ammonia, dry hydrochloric acid, dilute mineral acids, or aqueous alkalis (Husemann).

*Combinations. With Water?* Solutions of carotin in imperfectly dehydrated bisulphide of carbon or benzene deposit a white efflorescent body, which splits up, on the slightest warmth, into water and carotin, part of the carotin becoming sulphur-yellow and amorphous. More permanent crystals, perhaps of a second hydrate, are obtained, together with carotin, from the bisulphide solution to which absolute alcohol has been added: they form thin colourless laminæ, a solution of which in benzene deposits distinct six-sided prisms (Husemann).

Carotin is insoluble in *water* and in aqueous *alkalis* and *acetic acid* (Wackenroder). Its alcoholic solution is not precipitated by metallic salts, but is coloured darker and greenish by sesquichloride of iron (Husemann).

Carotin is easily soluble in *bisulphide of carbon*. It is scarcely soluble in boiling dilute or absolute *alcohol*, but more freely so in presence of hydrocarotin or fat oils. Amorphous carotin is soluble in alcohol. Difficultly soluble in *ether* and *chloroform*, and easily soluble in *benzene* and in *fixed* and *volatile oils*.

*Chlorine-nucleus* C³⁶Cl⁴H²⁰.

## Quadrichlorcarotin.

$$C^{36}Cl^4H^{20}O^2 = C^{36}Cl^4H^{20},O^2?$$
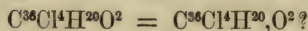
HUSEMANN. *Diessertation über Carotin, &c.* Gött. 1860.

Carotin exposed for some time to the action of dry chlorine, takes up about 55·86 p. c. of its weight (4 at. Cl = 54 p. c.), and becomes whitish-yellow and almost completely soluble in alcohol. From the alcoholic solution water precipitates quadrichlorcarotin as a white powder containing 37·06 p. c. chlorine (calc. = 36·04 Cl). It turns dark-red and soft at 100°, and melts at 120°. Easily soluble in bisulphide of carbon, ether, and benzene.

*Primary Nucleus* $C^{36}H^{26}$; *Oxygen-nucleus* $C^{34}H^{20}O^6$.

# Alkanet-red.

$$? \ C^{35}H^{20}O^8 \ = \ C^{36}H^{20}O^6,O^2.$$
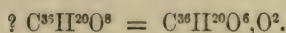
PELLETIER. *J. Phys.* 79, 278; *Bull. Pharm.* 6, 445. — *Ann. Chim. Phys.*
   51, 191; *Schw.* 67, 87; *Ann. Pharm.* 6, 27.
JOHN. *Chem. Schriften* 4, 81.
BOLLEY & WYDLER. *Ann. Pharm.* 62, 141.

*Acide anchusique* (Pelletier). *Pseudalkannin* (John). *Anchusin.* — Preisser's
statements were contradicted by Bolley (*Ann. Pharm.* 62, 133). — The colouring
matter of the roots of *Anchusa tinctoria* (*Handbuch* viii, *Phytochem.* 58).

*Preparation.* 1. The chopped roots are exhausted in a percolator
with cold water, which takes up a brown substance; they are then
dried and exhausted with alcohol. The alcoholic extract, after addi-
tion of a few drops of hydrochloric acid, to prevent the conversion of
the red into alkanet-green, is first distilled and then evaporated over
a water-bath, till a thick opaque liquid remains, from which the greater
part of the colour is already deposited; the liquid is shaken with
ether, which assumes a dark-red colour, and with water; and after
removing the aqueous layer, the ethereal solution is repeatedly shaken
with fresh water, until it is reduced in bulk and becomes syrupy. On
evaporation the alkanet-red is left behind (Bolley & Wydler). —
2. Coarsely powdered alkanet roots are exhausted with bisulphide of
carbon; the extract is freed from the bisulphide, partly by distillation
and completely by evaporation over a water-bath; the residue is
treated with cold water containing 2 p. c. of caustic soda; and the fine
indigo-blue solution is filtered and precipitated with a slight excess of
hydrochloric acid, which throws down the alkanet-red as a red-brown
precipitate. This is washed with water, collected, pressed, and dried.
The mass thus obtained forms a purple-red powder when triturated,
and colours fat very deeply (Lepage, *Polyt. Centr.* 1859, 751; *Chem.
Centr.* 1859, 397). — Pelletier either exhausts the roots with boiling
alcohol and evaporates, and dissolves the residue in ether, or exhausts
the root with ether and evaporates the extract.

*Properties.* Dark red-brown, resinous, brittle mass, slightly heavier
than water, melting below 60° without decomposition. When
cautiously heated, it volatilises in violet-red vapours resembling those
of iodine, having a penetrating odour, and sublimes in very light
flocks; a part, however, is decomposed (Pelletier). According to Pelletier
it has an acid reaction; according to Bolley & Wydler it has not.

| *Calculation according to* Gmelin. | | | Pelletier. | Bolley & Wydler. |
|---|---|---|---|---|
| 36 C ................. 216 | ...... | 72·00 | 69·85 | 71·33 |
| 20 H ................. 20 | ........ | 6·67 | 6·93 | 7·00 |
| 8 O ................. 64 | ........ | 21·33 | 23·22 | 21·67 |
| $C^{36}H^{20}O^8$ ............ 300 | ........ | 100·00 | 100·00 | 100·00 |

Pelletier's formula is $C^{17}H^{10}O^4$; that of Bolley & Wydler $C^{35}H^{20}O^5$.

*Decompositions.* **1.** Alkanet-red, submitted to *dry distillation*, yields a combustible gas and water, together with aromatic and empyreumatic oils. — **2.** *Chlorine* passed into the alcoholic solution colours it dirty yellow, and throws down yellow flocks soluble in alcohol. — **3.** Concentrated *nitric acid* converts it into oxalic acid and a small quantity of a bitter substance. — **4.** The alcoholic solution mixed with water and boiled is quickly coloured blue-green (Pelletier). Pure alkanet-red dissolved in alcohol remains unchanged after boiling for four hours, but, on addition of a little ammonia or of the nitrogenous brown substance of the roots, it is converted into alkanet-green (Bolley & Wydler).

Alkanet-green is obtained by evaporating the alcoholic tincture of the roots without addition of hydrochloric acid, the change of colour appearing soon after boiling commences. The extract is evaporated to dryness over a water-bath; the black-green residue is washed with water, which becomes coloured by a brown nitrogenous substance, and then exhausted with ether, which takes up a large quantity of a fine green colouring matter. Alkanet-green contains 70·08 p. c. C., 7·60 H., and 22·32 O., corresponding to the formula C$^{34}$H$^{22}$O$^8$ (calc. 70·34 p. c. C., 7·64 H.), and is formed from alkanet-red by the elimination of carbonic acid. According to Bolley & Wydler thus : C$^{35}$H$^{20}$O$^8$ + 2HO = C$^{34}$H$^{22}$O$^8$ + CO$^2$. — The brown nitrogenous substance is easily soluble in water, especially when hot, but insoluble in ether and strong alcohol. Its aqueous solution is rendered darker by alkalis, and precipitates metallic salts. By slow evaporation in the air, it acquires an acid reaction. It contains 40·05 p. c. C., 4·32 H., 3·12 N., and 52·51 O. (Bolley & Wydler).

Alkanet-red is insoluble in *water*. — It dissolves in *oil of vitriol* with amethyst-red colour (John).

Dissolves in aqueous *ammonia* and in *alkalis* with blue colour, and is precipitated by acids in brown-red flocks. *Baryta-*, *strontia-*, and *lime-water* also form blue compounds only slightly soluble in water, but, like the compounds with alkalis and metallic oxides, soluble in alcohol and ether (Pelletier). — *Chloride of tin* (proto-salt?) throws down from alcoholic alkanet-red a scarlet-red precipitate (John); *bichloride of tin* colours it violet without forming a precipitate (Bolley & Wydler). — Alcoholic alkanet-red does not precipitate alcoholic *neutral acetate of lead;* but from the alcoholic solution of the *basic acetate* it throws down a grey-blue precipitate somewhat soluble in alcohol. — It colours *sesquichloride of iron* deep olive-green, with slight precipitation (Bolley & Wydler). — *Mercuric chloride* precipitates the alcoholic solution flesh-coloured : other metallic salts, alum, for example, precipitate it only on account of the water they contain, the precipitates being therefore quite soluble in alcohol (Pelletier).

Alkanet-red dissolves in *alcohol*, and more easily in *ether*. It is soluble in *volatile oils* and *fats*, with fine red colour (Pelletier).

*Appendix to Alkanet-red.*

## 1. Chica-red.

Boussingault.  *Ann. Chim. Phys.* 27, 315 ; *Berzel. Jahresber.* 5, 251.
O. L. Erdmann.  *J. pr. Chem.* 71, 198 ; *Dingl.* 147, 467 ; *Chem. Centr.* 1857, 753 ; *Chem. Gaz.* 1857, 465 ; *Kopp's Jahresb.* 1857, 487.

*The resinous red of Bignonia Chica.* — The colouring principle of the dye-stuffs known in commerce as *Chica, Carajuru,* or *Carucru.*

Carajuru is obtained by the natives of Guiana and Brazil from the leaves of *Bignonia Chica.* The bruised leaves are steeped in water and set aside till fermentation takes place, during which the red colour is thrown down. The precipitation is accelerated by the introduction of a bark into the liquid. The colour is washed, dried in the sun, and made into balls. — Carajuru occurs in the form of blood-red cakes, six or eight inches in diameter, and three to four inches thick, resembling, except in point of colour, pieces of indigo. It is a mixture of chica-red, vegetable cellular matter, and mineral substances. See also Hancock, (*Ed. N. Phil. J.* 7, 283), and Virey (*N. J. Pharm.* 5, 151), on carajuru.

Chica-red is obtained from carajuru by boiling with alcohol and evaporating the tincture, when it is left as an amorphous, brownish, shining mass (Boussingault). This mass is digested in ether till it imparts only a light yellow colour thereto, and the undissolved portion is dried over oil of vitriol (*a*); or the colouring matter is extracted with alcohol containing sulphuric acid ; the solution neutralised with carbonate of ammonia ; and the precipitate washed with boiling water and dried at 100° (*b*) (Erdmann).

Chica-red obtained according to *a* contains 59·62 p. c. carbon, 5·34 hydrogen, and 35·04 oxygen ; that prepared according to *b* contains, on an average, 63·10 p. c. carbon, 4·94 hydrogen, and 31·96 oxygen ; *a* corresponds therefore to the formula $C^{16}H^{9}O^{7}$ ; *b* to the formula of anisic acid, $C^{16}H^{8}O^{6}$, with which chica-red is isomeric (Erdmann).

Carajuru exposed to *light* assumes a brown-red, and at last a cinnamon-brown colour (Erdmann). Chica-red is decomposed by *heat,* puffing up, evolving yellow fumes, and leaving a difficultly combustible charcoal. — *Chlorine* turns it brown and decomposes it. — Cold *oil of vitriol* blackens it without setting free sulphurous acid ; water added thereto dissolves a portion and leaves a black residue, which again turns red in a few days under water (Boussingault). — Chica-red, warmed with *nitric acid*, is pretty quickly converted into anisic acid, without any considerable evolution of red vapours. The reaction is attended with the emission of an odour of hydrocyanic acid (Erdmann). Carajuru treated with nitric (or chromic) acid, also yields principally anisic acid, together with picric and oxalic acids.

When carajuru is digested with *potash, grape-sugar,* and water or alcohol, in a closed flask, according to the method described under INDIGO (xiii, 39, 7), a violet solution, immediately turning brown in the air, is produced, from which hydrochloric acid free from air throws down a red-yellow precipitate (Erdmann).

Chica-red is insoluble in *water.* — Carajuru gives up its colouring matter to *hydrochloric acid*, forming a dark brown-yellow solution. With warm dilute *sulphuric acid* it forms a yellow to orange solution, which deposits yellow-red, amorphous granules on cooling, and gives, with ammonia, a dark purple-red precipitate (Erdmann). — Chica-red is soluble in *ammonia*, and is precipitated from the solution by hydrochloric acid with yellowish-brown colour (Erdmann). It dissolves quickly and completely in *caustic potash* and *carbonate of potash*, the solution having the colour of wine-lees, and is again precipitated by acids (Boussingault). According to Erdmann, carbonate of ammonia and carbonate of soda extract hardly any colour from carajuru ; according to Boussingault, carbonate of potash takes up the whole of the

colouring matter. — Aqueous, and more especially alcoholic potash, take up the colouring matter of carajuru in large quantity, the latter assuming a deep blood-red colour (Erdmann).

Chica-red dissolves easily in *alcohol* : the ruby-red solution forms no deposit on cooling, and is precipitated by water only after concentration (Boussingault). It dissolves slightly in *ether* with yellow colour (Erdmann). *Acetic acid* is coloured dark-yellow by it, and deposits a portion with carmine-red colour on standing. The red dissolves slightly in *oil of turpentine* with brown colour, but is insoluble in *castor, olive,* and *neat's-foot oil,* with which, however, it forms a very intimate carmine-red mixture (Boussingault).

2. *Red colouring matter of the root-bark of Lithospermum arvense.* — Extracted from the bark by alcohol containing acetic acid. The greater part of the alcohol is distilled off, and the remainder is evaporated over the water-bath; the black mass which separates from the aqueous residue is collected and treated while still moist, with ether, which dissolves nearly the whole; and the ethereal solution is then filtered and evaporated. The black, resinous colouring matter thus obtained is not perfectly dried even by prolonged heating in a steam-bath; it dries better after treatment with a concentrated solution of carbonate of soda, by which a small portion is dissolved with blue colour, precipitable in red flocks by dilute sulphuric acid. — The colouring matter dissolves in oil of vitriol with fine red colour, and is precipitated from the solution by water with green coloration. It is quickly decomposed by nitric acid. It dissolves in ether with blue colour, and in alcohol with violet colour, which is turned blue by alkalis (Ludwig & Kromayer, *N. Br. Arch.* 96, 271 ; *Chem. Centr.* 1859, 87).

3. *Resinous red of Spanish pepper.* — The extract, prepared with boiling alcohol, is exhausted with water and cold alcohol in succession, the red colour being thus left behind. — It dissolves in hot caustic potash-solution, and is precipitated blood-red by acids. Not perceptibly soluble in cold alcohol; the solution in hot alcohol deposits it in flocks on cooling (Braconnot, *Ann. Chim. Phys.* 6, 124).

# 4. Nucin.

A. Vogel, Jun., & Reischauer. *N. Repert.* 5, 106. — Further 7, 1 ; abstr. *N. Jahrb. Pharm.* 9, 328 ; *J. pr. Chem.* 73, 319.

The (altered) colouring matter of green walnut-shells was examined by Braconnot (*Ann. Chim.* 74, 305), and J. A. Buchner (*Repert.* 79, 355), the latter of whom distinguished a *Juglandic acid* and a *Walnut-brown.*

*Source.* In the green shells of walnuts. The nucin occurs ready formed, but is accompanied by another body, allied to pyrogallic acid, which readily decomposes the nucin when exposed to the air. — The unripe nuts, shelled about the end of June, become covered, on exposure to the air, with small yellow crystalline needles of nucin, which may also be detected in the cells of the shell under the microscope. Most solvents, as ether, alcohol, chloroform, and oil of turpentine,

extract the nucin from the shells, but leave it on evaporation in a changed state in the form of a dark resin, from which nucin can no longer be obtained by sublimation Rectified benzene or sulphide of carbon only, when left for a short time in contact with the shells, yields on evaporation crystals of nucin, which, however, easily undergo alteration when benzene is the solvent used. — But if the substance accompanying the nucin be first decomposed by shaking the ethereal extract with nitrate of silver (or nitrate of copper), whereby metallic silver is thrown down, the ethereal layer, when afterwards evaporated, yields nucin, which does not suffer change. — The substance which decomposes the nucin may be obtained in the following manner. Walnut-shells are digested with alcohol, and the tincture is removed, whereupon it exhibits a yellow colour, before turning green or brown, and immediately precipitated with neutral acetate of lead; the white precipitate, separated by filtration, is then decomposed by hydrosulphuric acid; and the filtrate is evaporated, an acid gum having a harsh taste, being left behind. This substance, in contact with nucin, turns it brown and decomposes it.

*Preparation.* The separated and somewhat comminuted shells are digested for two hours in ether, and the decanted tincture is shaken up with an aqueous solution of nitrate of copper containing a slight excess of hydrated oxide of copper, until a pure blood-red coloration appears; the ethereal layer is then removed and allowed to evaporate over oil of vitriol. (When evaporated in the air, the nucin turns brown and undergoes decomposition.) Part of the nucin remains dissolved in the aqueous nitrate of copper; it may be set free by the cautious addition of nitric acid till the red colour of the solution is changed to blue-green, and can then be taken up by ether. — The nucin thus obtained is mixed with quartz-sand and heated to 80° or 90° in a sand-bath placed within a water-bath, when, on continued heating for a week, an abundant sublimate is obtained.

*Properties.* Reddish-yellow, strongly lustrous, very brittle needles, half an inch long; or small, apparently quadratic prisms, volatile without decomposition, and containing no nitrogen.

Nucin is insoluble in *water.* It dissolves abundantly in aqueous *ammonia*, in aqueous *caustic alkalis*, in *borates* and *phosphates* of the alkalis, and in *basic acetate of lead* with splendid purple-red colour, and is precipitated by acids in brown-red flocks.

It dissolves with difficulty in *alcohol*, easily in *ether.*

*Oxygen-nucleus* $C^{36}H^{16}O^{10}$.

## Cetraric Acid.

$$C^{36}H^{16}O^{16} = C^{36}H^{16}O^{10}, O^5.$$
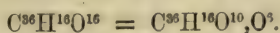
BERZELIUS. *Schw.* 7, 317.

HERBERGER. *Repert.* 36, 226; 56, 273; 58, 271. — *Ann. Pharm.* 21, 137.

SCHNEDERMANN. *Ann. Pharm.* 54, 143.

SCHNEDERMANN & KNOP.  *Ann. Pharm.* 55, 144; *J. pr. Chem.* 36, 107.

*Cetrarin.*  Discovered by Herberger, but first obtained pure by Schnedermann & Knop.

*Sources.*  In Iceland moss (*Cetraria islandica*). — *Sticta pulmonacea* contains a similar bitter substance, Knop and Schnedermann's *stictic acid*, which has not been further investigated (*J. pr. Chem.* 39, 367).

*Preparation.*  Iceland moss is boiled in alcohol with addition of carbonate of potash, and the decoction is strained and precipitated with dilute hydrochloric acid and water.  The precipitate, which contains cetraric acid. lichenic acid (xvi, 195), tallochlor and other substances, is exhausted, first with boiling alcohol of 42 to 45 p. c., and afterwards with ether holding oil of rosemary or camphor in solution. From the residual grey-white mixture of cetraric acid and an indifferent white body, the acid is taken up by cold aqueous bicarbonate of potash, and at once precipitated from the alkaline solution by hydrochloric acid.  It is purified by crystallisation from the smallest possible quantity of alcohol. — A portion of the cetraric acid is taken up by the weak alcohol, and evaporates, together with the lichenic acid, on cooling.  The latter substance is extracted by boiling rock-oil as described at xvi, 195, and the undissolved cetraric acid is then purified with bicarbonate of potash.  A further portion of the cetraric acid dissolves in ether containing oil of rosemary, and crystallises therefrom tolerably pure on partially distilling the solution and cooling (Schnedermann & Knop). — Cetraric acid may also be obtained by precipitating an alkaline decoction of Iceland moss with hydrochloric acid, washing the precipitate with a cold mixture of oil of rosemary and ether, and exhausting the residue with bicarbonate of potash (Schnedermann & Knop).

Herberger digests Iceland moss for an hour, at a temperature of 60–70°, in 4 pts. of alcohol of sp. gr. 0·83, decants, presses the residue, and exhausts it twice with cold water.  The clear alcoholic liquid, when added to the aqueous infusion, deposits greenish-white flocks, from which alcohol takes up a little cetrarin.  The filtrate, mixed with sulphuric acid, throws down cetrarin, which is collected, pressed, and treated, while still moist, with ether or alcohol of sp. gr. 0·83, which takes up leaf-green and a little cetrarin.  The remainder, on boiling with 200 pts. of absolute alcohol, is dissolved (with the exception of some inorganic salts), and the filtrate, when cooled and concentrated, yields pure cetrarin.

The following substances are also obtained in the preparation of cetraric acid.

a. *Tallochlor.*  The green colouring matter of Iceland moss.  It is taken up by the ether and oil of rosemary used for washing cetraric acid. After crystallising out the cetraric acid taken up at the same time, the solution is evaporated to dryness, and the residue is dissolved in boiling alcohol, diluted with water till the alcohol is reduced to 42-45 p. c., and filtered boiling.  By this process, repeated several times, the lichenic acid is removed, and the residue is then treated with boiling rock-oil, which dissolves tallochlor and fat, whilst cetraric acid and brown substances are left behind.  The solution, after addition of water, is submitted to distillation; the residue is dried till the rock-oil is completely volatilised, and afterwards dissolved in alcohol; and the

tallochlor is precipitated either by digestion with hydrate of lime, or better by alcoholic neutral acetate of lead. The green flocks thus produced are boiled with ether, and freed from oxide of lead by means of acetic acid, — Brittle, friable, green mass, insoluble in water, and nearly insoluble in hydrochloric acid, but soluble in strong alcohol, ether, and volatile and fixed oils (Schnedermann & Knop).

b. *A yellowish-white, indifferent body.* Remains behind on dissolving cetraric acid in bicarbonate of potash, and is purified by washing with water and crystallising from alcohol. — Inodorous, tasteless. After deducting 0·2 to 0·3 p. c. of ash, it contains 67·39 to 70 p. c. carbon, 10·82 to 11·23 hydrogen, and 0·51 nitrogen. — Insoluble in water, acids, alkalis, ether, and oils. Dissolves with difficulty in boiling alcohol, the solution becoming turbid and slimy on cooling (Schnedermann & Knop).

*Properties.* Cetraric acid forms a snow-white, loose network of delicate shining crystals, appearing under the microscope as long needles. It is not volatile, and cannot be melted without decomposition. Very bitter. Does not lose water at 100° (Schnedermann & Knop). Herberger's cetrarin forms a white powder resembling magnesia, permanent in the air, inodorous, and neutral.

|  |  |  |  |  | Knop & Schnedermann. |
|---|---|---|---|---|---|
|  | At 100. |  |  |  | *mean.* |
| 36 C | 216 | ........ | 60·00 | ........ | 60·05 |
| 16 H | 16 | ........ | 4·44 | ........ | 4·67 |
| 16 O | 128 | ........ | 35·56 | ........ | 35·28 |
| $C^{36}H^{16}O^{16}$ | 360 | ........ | 100·00 | ........ | 100·00 |

According to Knop and Schnedermann it is $C^{34}H^{16}O^{15}$; according to Hlasiwetz (*Wien. Acad. Ber.* 20, 208) $C^{34}H^{15}O^{15}$.

*Decompositions.* 1. The solutions of cetraric acid in aqueous ammonia and in the alkalis absorb *oxygen* from the air, especially when heated, acquiring at the same time a brown colour, and losing their bitter taste. — When cetraric acid is boiled in caustic potash, with access of air, till the bitter taste has completely disappeared, and the solution is precipitated with hydrochloric acid, the brown precipitate (*lichenulmic acid* of Knop & Schnedermann), dried at 80°, contains 60·7 p. c. C., 4·3 H., and 35 O.; it dissolves slightly in water, and combines with bases: when dissolved in ammonia and dried over oil of vitriol, it leaves a dark-brown mass, which is soluble in water and precipitates the salts of the earth-metals and heavy metals (Knop and Schnedermann, *J. pr. Chem.* 40, 393.)

Cetrarin turns brown at 125°, and when more strongly *heated* gives off a red-yellow acid oil, which solidifies in the cold: at 160° it blackens and ultimately leaves a large quantity of porous charcoal. — By long boiling with *water* it is coloured brown. — Concentrated *nitric acid* converts it into a yellow-brown resin and oxalic acid, with evolution of nitric oxide. *Phosphoric acid* gradually converts it into ulmin. — *Oil of vitriol* colours it first yellow, then brown, and dissolves it with red-brown colour changing to dark blood-red: water throws down ulmin from the solution. — Aqueous *hydrochloric acid* gently warmed with cetrarin converts it into *cetrarin-blue,* which remains behind on evaporation, as a light green-blue bitter mass This last substance is quickly

converted into ulmin by alkalis, and dissolves in oil of vitriol with dark blood-red colour: it is coloured a fine carmine-red by concentrated nitric acid, dissolves with yellow colour in a large quantity of the acid, and is precipitated by water at first unchanged. — When hydrochloric acid gas is passed over cetrarin, there is no absorption in the cold, and no formation of cetrarin-blue; but on heating, the cetrarin becomes carbonised, with formation of a yellow-red liquid and a carmine-red, semi-solid mass (Herberger).

*Combinations.* Cetraric acid is almost absolutely insoluble in *water;* water boiled with it acquires a faintly bitter taste (Knop & Schnedermann). — Cetrarin dissolves very slightly in *bisulphide of carbon* (Herberger).

It dissolves very readily in aqueous *alkalis* and their *carbonates*; the bright yellow solutions have a very bitter taste, and are precipitated by acids.  Respecting their alteration in contact with the air, see above. — Alcoholic cetrarin precipitates most metallic salts (Herberger).

*Cetrarate of Ammonia.* — Solutions of the acid in aqueous ammonia turn brown in the air and on evaporation.  When cetraric acid is boiled with alcohol and solid carbonate of ammonia, and the yellow filtrate is concentrated by rapid boiling in flasks, a small quantity of the ammonia-salt separates from the red-yellow liquid, on cooling, in the form of a yellow micro-crystalline powder; most of the salt remains, however, in the mother-liquor, and undergoes further changes. — In dry gaseous ammonia, free from air, cetraric acid becomes hot, assumes a lemon-yellow colour, and takes up 10·2 p. c, of its weight of ammonia, forming the salt $2NH^3,C^{36}H^{16}O^{16}$ (calc.  9·44 p. c. $NH^3$).  The salt smells slightly of ammonia, but loses this smell over oil of vitriol, and then forms with water a fine yellow neutral solution (Knop & Schnedermann).

*Cetrarate of Lead.* Formed by precipitating the neutral ammonia-salt with neutral acetate of lead. — Yellow flocks insoluble in water. — The precipitate produced by alcoholic neutral acetate of lead in an alcoholic solution of cetraric acid contains varying proportions (38·7 to 44·4 p. c.) of oxide of lead (Schnedermann & Knop).

|  |  |  |  | Schnedermann & Kopp. |
|---|---|---|---|---|
| 36 C | 216 | ........ | 38·19 | ........ 36·29 |
| 14 H | 14 | ........ | 2·48 | ........ 2·78 |
| 14 O | 112 | ........ | 19·80 | ........ 21·20 |
| 2 PbO | 223·6 | ........ | 39·53 | ........ 39·73 |
| $C^{36}H^{14}Pb^2O^{16}$ | 565·6 | ........ | 100·00 | ·........ 100·00 |

The salts of the alkalis precipitate *ferric salts* brown-red, or in more dilute solutions, blood-red. — Cetrarate of *silver* is a yellow precipitate, quickly turning brown (Schnedermann & Knop).

Cetraric acid dissolves with difficulty in cold, easily in boiling strong *alcohol.*  It dissolves slightly in ether, but not in *fixed* or *volatile oils* (Schnedermann & Knop).  It does not combine with *urea* (Hlasiwetz).  Alcoholic cetrarin is not precipitated by *gallic* or *tannic acid* (Herberger).

*Oxyazo-nucleus* $C^{36}NH^{19}O^6$.

## Pelosine.

$$C^{36}NH^{21}O^6 = C^{36}NH^{19}O^6,H^2.$$
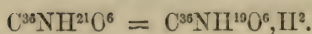
Wiggers.   *Ann. Pharm.* 33, 81 ; Prelim. Notice, *Ann. Pharm.* 27, 29.
Bödeker.   *Ann. Pharm.* 69, 53 ; *Pharm. Centr.* 1849, 150 ; *Chem. Gaz.* 1849, 152 ; *Lieb. Kopp's Jahresb.* 1849, 385.
Gr. Williams.   *Chem. Gaz.* 1858, 321 ; *J. pr. Chem.* 76, 382 ; *Kopp's Jahresb.* 1858, 375.

*Cissampeline.* — Discovered by Wiggers, and specially investigated by Bödeker. — Occurs in *Radix Pareiræ bravæ*, the root of an American menispermaceous plant, *Cissampelas Pareira*.

*Preparation.* The sliced or bruised roots are boiled four times in water containing sulphuric acid, and the brown decoction is filtered. When it is quite cold, carbonate of soda, not in excess, is added, and the bulky grey-brown precipitate thereby produced is washed, dried, dissolved in water containing sulphuric acid, and treated with animal charcoal. The filtered solution is again precipitated with carbonate of soda ; the now dirty-yellow precipitate is washed and dried completely at 100°, and afterwards powdered and exhausted with ether, which takes up pelosine. Water in the precipitate. or in the ether, prevents the solution of pelosine. Alcohol takes up other substances at the same time. The colourless ethereal solution yields, on evaporation, anhydrous pelosine, which is coloured yellow by some decomposition-product formed during concentration (Wiggers). If the ethereal solution is not quite colourless, it must be evaporated, and the foregoing process of solution in acid, precipitation with carbonate of soda, and exhaustion of the dried precipitate with ether, repeated (Wiggers).

*Properties.* Yellowish, transparent, amorphous varnish, triturable to a white powder (Wiggers, Bödeker). In the moist state, or in solution, it turns litmus blue. Has a nauseous, sweetish, bitter taste (Wiggers).

|        |        | At 120°. |        |        | Bödeker. mean. |
| ------ | ------ | -------- | ------ | ------ | -------------- |
| 36 C   | ...... | 216      | ...... | 72·24  | ...... 71·93   |
| N      | ...... | 14       | ...... | 4·68   |                |
| 21 H   | ...... | 21       | ...... | 7·02   | ...... 7·13    |
| 6 O    | ...... | 48       | ...... | 16·06  |                |
| $C^{36}NH^{21}O^6$ | ...... | 299 | ...... | 100·00 |          |

*Decompositions,* 1. Pelosine, when *heated*, melts easily, turns brown, puffs up, evolves an odour of burning bread, and burns with a bright, smoky flame, leaving a light, difficultly combustible charcoal (Wiggers). — 2. Moist or dissolved pelosine, but not the perfectly dry substance, is decomposed by exposure to air and light, with especial rapidity in presence of alkalis, with formation of a brown decomposition-product, insoluble in ether, but soluble in alkalis (Wiggers), and of Bödeker's *pelluteine.* The decomposition is accompanied by evolution of ammonia

(Bödeker). — 3. Pelosine dissolves in weak *nitric acid* without decomposition. Nitric acid of sp. gr. 1·25, or higher, converts it, on warming, into a tough, brown-yellow, resinous mass, insoluble in pure water, or in water containing nitric acid, probably the same body that is produced on exposing pelosine to the air (Wiggers). — 4. Pelosine distilled with *caustic potash* yields methylamine, bimethylamine, pyrrhol (xv, 5), and combustible gases (Gr. Williams).

*Combinations.* — *With Water.* — *Hydrated Pelosine.* Pelosine takes up water or aqueous vapour very rapidly (Bödeker). When the ethereal solution is poured upon water, and the ether is distilled off, hydrated pelosine remains floating on the water in the form of a white powder. On shaking the ethereal solution with water, the hydrate separates at the surface of contact of the two layers of liquid (Wiggers). — Nearly white, amorphous powder (Wiggers). After drying over oil of vitriol it loses, at 120°, 8·21 p. c. = 3 at. water (calc. = 8·28 p. c. HO) (Bödeker).

Pelosine is insoluble, or nearly so, in *water* either cold or boiling (Wiggers).

Pelosine neutralises *acids* completely. The salts are not crystallisable; the hydrochlorate alone, according to Wiggers, forms small nodules. From the aqueous solutions of the salts, ammonia, and caustic alkalis and their carbonates, throw down hydrated pelosine as a bulky white precipitate, easily soluble in excess of potash, but difficultly soluble, or insoluble, in excess of the other precipitants. The salts of pelosine give abundant white precipitates with phosphate of soda, and with protochloride of tin (Wiggers).

*Hydrochlorate of Pelosine.* — Dry hydrochloric acid gas is passed into a solution of dry pelosine in ether free from water and alcohol, till the solution has an acid reaction. The white flocks produced are quickly thrown on a filter, and washed continuously with absolute ether, so long as any acid is thereby removed, and the filter is at once placed in a receiver over oil of vitriol. — Snow-white powder, which absorbs water with avidity, and cakes together to an amber-coloured mass. Dissolves easily in water and in alcohol without colour, and remains behind, on evaporation, as an amorphous varnish. — The salt, exposed to moisture, and afterwards dried over oil of vitriol, loses 5·08 p c. of water at 110° (2 at. = 5 24 p. c. HO) (Bödeker).

|  |  | Dried. |  |  |  | Bödeker. mean. |
|---|---|---|---|---|---|---|
| 36 C | ............ | 216 | ........ | 64·38 | ........ | 63·69 |
| N | ............ | 14 | ........ | 4·17 | ........ | 4·08 |
| 22 H | ............ | 22 | ........ | 6·55 | ........ | 6·59 |
| 6 O | ............ | 48 | ........ | 14·32 | ........ | 14·56 |
| Cl | ............ | 35·5 | ........ | 10·58 | ........ | 11·08 |
| C³⁶NH²¹O⁶,HCl | ........ | 335·5 | ........ | 100·00 | ........ | 100·00 |

Pelosine does not combine with perchloric acid (Bödeker, *Ann. Pharm.* 71, 63).

*Chromate of Pelosine.* — Hydrochlorate of pelosine is precipitated by bichromate of potash in bright yellow flocks, which become dirty yellow-brown when washed, and assume a still darker colour on drying in a vacuum. — At 80° the salt quickly becomes dark-brown, and a

little over 100° evolves an odour of chinoline and carbolic acid, whilst sesquioxide of chromium and charcoal remain behind (Bödeker). See also (p. 26) the decomposition of pelosine by caustic potash, according to which Williams regards the formation of chinoline as improbable.

| | | Over oil of vitriol. | | | Bödeker. mean. |
|---|---|---|---|---|---|
| 36 C | .......................................... | 216·0 | ........ | 58·81 ........ | 58·99 |
| N | ......... ............................ | 14·0 | ........ | 3·81 | |
| 23 H | .......................................... | 23·0 | ........ | 6·26 ........ | 5·55 |
| 8 O | ................. ........................ | 64·0 | ........ | 17·42 | |
| CrO³ | .................................... | 50·3 | ........ | 13·70 ........ | 14·54 |
| $C^{36}NH^{21}O^6,CrO^3$ + 2aq. | ........ | 367·3 | ........ | 100·00 | |

*Chloride of gold* forms with pelosine-salts, a dirty-yellow precipitate, the supernatant liquid quickly assuming a violet colour and depositing gold (Wiggers).

*Chloroplatinate of Pelosine.* — Alcoholic hydrochlorate of pelosine is precipitated by bichloride of platinum, and the pale-yellow precipitate is washed with alcohol and water, whereby it acquires a brown colour at the edges. — Amorphous, strongly electric powder. After drying over oil of vitriol, it does not lose weight at 110°. When more strongly heated, it melts and swells up strongly, emitting a repulsive, penetrating odour (Bödeker).

| | | At 100°. | | | Bödeker. |
|---|---|---|---|---|---|
| 36 C | ................................ | 216·0 | ........ | 42·79 ........ | 43·50 |
| N | ................................ | 14·0 | ........ | 2·77 | |
| 22 H | ................ ............... | 22·0 | ........ | 4·35 ........ | 4·88 |
| 6 O | ................................ | 48·0 | ........ | 9·50 | |
| Pt | ................................ | 98·7 | ........ | 19·53 ........ | 19·48 |
| 3 Cl | ................................ | 106·5 | ........ | 21·06 | |
| $C^{36}NH^{21}O^6,HCl,PtCl^2$ | ...... | 505·2 | ........ | 100·00 | |

The salts of pelosine give an abundant white precipitate with *tannic acid* (Wiggers).

Pelosine dissolves very easily in *alcohol*, and is precipitated from the solution by water as a hydrate. — It dissolves slowly, but abundantly, in *ether*. In ether containing water it is converted into the hydrate, which is insoluble in ether (Wiggers).

## Appendix to Pelosine.

# Pelluteine.

BÖDEKER. *Ann. Pharm.* 69, 59.

*Formation* (p. 25.)

Hydrated pelosine is exposed to air and light until, after drying, it is no longer soluble in absolute ether, and to convert the remainder into pelluteine it is boiled repeatedly with water in a shallow basin. The dried substance is boiled with absolute alcohol, and the solution filtered from brown flocks of humus, when, on cooling, the pelluteine is deposited in pale brown-yellow flocks, which are to be washed with cold alcohol.

Pelluteine contains, at 110°, 73·88 p. c. C., 3·84 N., 6·18 H., and 16·10 O.; in the platinum double-salt, 17·84 p. c. Pt., whence Bödeker deduces the formula $C^{42}NH^{21}O^7$; Gerhardt (*Traité* 4, 230), the formula $C^{36}NH^{19}O^6$.

Pelluteine behaves towards *acids* in the same manner as pelosine. It forms dark-yellow precipitates with various reagents. It is insoluble in *ether*.

## Codeine.

$$C^{36}NH^{21}O^6 = C^{36}NH^{19}O^6, H^2.$$
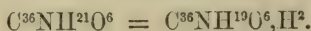
Robiquet.   *J. Chim. méd.* 9, 96; *J. Pharm.* 19, 87; *Ann. Chim. Phys.* 51, 259; *Ann. Pharm.* 5, 106; *Schw.* 67, 297; abstr. *Pogg.* 27, 650. — *N. J. Pharm.* 31, 10; *J. pr. Chem.* 72, 271.
Gregory.   *J. Pharm.* 20, 85.
Couerbe.   *Ann. Chim. Phys.* 59, 159.
Pelletier.   *J. Pharm.* 21, 557; *N. Br. Arch.* 5, 158; *Ann. Pharm.* 16, 27. — *Ann. Chim. Phys.* 63, 185; *Ann. Pharm.* 22, 132.
Regnault.   *Ann. Pharm.* 26, 25; *J. pr. Chem.* 16, 272.
Liebig.   *Ann. Pharm.* 26, 44.
Dollfus.   *Ann. Pharm.* 16, 215.
Anderson.   *Trans. Roy. Soc. Edin.* 20, 157; *Compt. chim.* 1850, 321; *Ann. Pharm.* 77, 341; *Pharm. Centr.* 1851, 337; *N. Ann. Chim. Phys.* 34, 493.

Discovered by Robiquet in 1832; particularly investigated by Anderson.

*Source.* In opium. Smyrna opium contains 0·62 to 0·86 per cent. (Mulder), 0·25 p. c. (Schindler); opium from Constantinople 0·52 p. c. (Schindler). Couerbe obtained from 40 pounds of opium 1½ ounces of codeine. Merck obtained from Smyrna opium ¼ p. c.; from Bengal opium ½ p. c.

*Preparation.* By treating opium according to the Robertson-Gregory method (xvi, 419), a mixture (or double-salt) of hydrochlorate of morphine and hydrochlorate of codeine is obtained, from an aqueous solution of which ammonia precipitates the greater part of the morphine. On concentrating the filtrate, hydrochlorate of codeine crystallises first. It is freed from most of the sal-ammoniac with which it is mixed by recrystallisation, dissolved in hot water, and decomposed by a concentrated solution of caustic potash, whereby a portion of the codeine is thrown down in the form of an oil, which afterwards solidifies, whilst another portion crystallises on cooling. The mother-liquor, when concentrated, deposits first a little more codeine, and afterwards crystals of morphine (Robiquet, Anderson). The codeine is purified by washing with cold water, dissolving in ether, and leaving the solution to evaporate, with addition of water, when hydrated codeine crystallises (Robiquet); or, the codeine is dissolved in hydrochloric acid, boiled with animal charcoal, again precipitated with caustic potash, and freed from morphine by solution in ether containing water (Anderson). — For other modes of preparation see xvi, 421, 422.

Winckler (*Repert.* 45, 459) frees the aqueous extract of opium from morphine by ammonia, from meconic acid by chloride of calcium, and

from colouring matter by basic acetate of lead. The filtrate is freed from lead by sulphuric acid, treated with an excess of caustic potash, and exposed to the air till the excess of potash is saturated with carbonic acid, after which it is agitated with ether. On evaporating the ethereal solution, there remains a yellowish, non-crystalline residue, which, after addition of hydrochloric acid, yields crystals of hydrochlorate of codeine.

Merck (*Ann. Pharm.* 11, 279) treats the mixture of morphine and codeine thrown down by caustic potash with cold alcohol, and neutralises the tincture cautiously with sulphuric acid. He then distils off the alcohol, dilutes the residue with water so long as cloudiness is produced, and evaporates the filtrate to a syrup. After cooling, the syrup is mixed with ether and an excess of caustic potash-solution, and shaken. The separated ethereal solution yields, after some hours, crystals of codeine, which are purified from adhering oil by solution in ether.

O. Henry (*J. Pharm.* 21, 222; abstr. *Ann. Pharm.* 15, 152) exhausts 3 ounces of opium with lukewarm water; concentrates the filtrate somewhat; precipitates morphine and narcotine by ammonia; and evaporates the filtrate, whereupon the greater part of the meconate of lime is thrown down. The precipitate produced (after filtering from the lime-salt) by infusion of galls is dissolved in alcohol, according to vii, 177, 3, and freed from tannic acid by means of neutral acetate of lead, and from excess of lead by hydrosulphuric acid. The filtrate is then evaporated, and the brown tarry residue is exactly neutralised with nitric acid. After two crystallisations, silky needles are obtained, from which potash throws down a white precipitate of codeine.

Solutions containing morphine, codeine, and opianyl, when acidified with hydrochloric acid, yield to ether only the last-named substance (Pelletier).

On the detection of codeine in cases of poisoning, see Stas (in the places mentioned, xvi, 424).

*Properties.* Codeine is obtained from ether in small, colourless, anhydrous crystals (Regnault, Anderson). Hydrated codeine crystallised from an aqueous solution loses its water of crystallisation at 100° (Anderson). — Codeine melts at 100° (Couerbe); at 150° and solidifies in the crystalline state on cooling (Robiquet). Hydrated codeine melts to an oil in boiling water, losing its water of crystallisation (Couerbe). — Codeine has a strongly alkaline reaction (Robiquet, Anderson). It is poisonous (Kunkel). In doses of 0·15 to 0·20 gramme, it produces a heavy, intoxicated sleep, with feeling of stupefaction, and sometimes nausea and vomiting on awaking; in doses of 0·020 to 0·03 grm. it is soothing (Robiquet). Compare Gregory (*J. Pharm.* 20, 85). —Lavo-rotatory: $[\alpha]_r = 118·2°$, scarcely altered by acids (Bouchardet & Boudet, *N. J. Pharm.* 23, 392; *Ann. Pharm.* 88, 213), and not affected by difference of temperature. The rotation is not in proportion to the amount of codeine in solution, and is not constant for different colours (Robiquet).

| | | *Anhydrous.* | | | Robiquet. | | Couerbe. |
|---|---|---|---|---|---|---|---|
| 36 C | 216 | ........ | 72·24 | ........ | 70·36 | ........ | 71·85 |
| N | 14 | ........ | 4·68 | ........ | 5·35 | ........ | 5·23 |
| 21 H | 21 | ........ | 7·02 | ........ | 7·59 | ........ | 7·15 |
| 6 O | 48 | ........ | 16·06 | ........ | 16·70 | ........ | 15·77 |
| $C^{36}NH^{21}O^{6}$ | 299 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

| | Regnault. | | Gregory. | | Will. | | Anderson. |
|---|---|---|---|---|---|---|---|
| C | 73·12 | ........ | 73·18 | ........ | 73·28 | ........ | 73·03 |
| N | 4·89 | ........ | 4·83 | ........ | | ........ | 4·50 |
| H | 7·21 | ........ | 7·24 | ........ | 7·25 | ........ | 7·05 |
| O | 14·78 | ........ | 14·75 | ........ | | ........ | 15·42 |
| | 100·00 | ........ | 100·00 | ........ | | ........ | 100·00 |

According to Regnault, the formula is C³⁵NH²⁰O⁵; according to Dollfus, C³⁴NH¹⁹O⁵. The above formula was proposed by Gerhardt (*Rev. Scient.*, 10, 202; *N. Ann. Chim. Phys.* 7, 253) and shown to be correct by Anderson. — Codeine contains 2 at. CH more than morphine, and is isomeric with pelosine (p. 25).

*Amorphous Codeine.* When a solution of codeine in excess of moderately concentrated sulphuric acid is warmed for some time (not however too long or too strongly), and is afterwards precipitated with carbonate of soda, a grey precipitate is produced, which, after washing, is to be dissolved in alcohol and again thrown down by water. It contains 71·92 p. c. carbon and 7·53 hydrogen (after prolonged treatment with sulphuric acid, 72·53 p.c. carbon, 6·84 hydrogen), and has therefore the same composition as codeine. It melts at 100° to a black resin, and is insoluble in water, but easily soluble in acids, forming amorphous salts, which dry up to a resinous mass on evaporation. Amorphous codeine dissolves easily in alcohol, and is precipitated from the solution by ether (Anderson).

*Decompositions.* 1. Melted codeine, when more strongly *heated*, creeps up the sides of the vessel without volatilising; on platinum-foil it burns with flame and leaves no residue (Robiquet). — 2. For the reaction with iodine, see below. — *Chloride of iodine* forms biniodocodeine (p. 36) (Brown). — 3. *Bromine-water* quickly dissolves codeine, and forms hydrobromate of bromocodeine having a characteristic red colour; the salt is converted by excess of bromine into hydrobromate of terbromocodeine, the greater part of which is thrown down in the form of powder (Anderson). — 4. *Chlorine* or *chlorine-water* forms with aqueous codeine a dark-brown liquid, from which ammonia precipitates an amorphous, basic resin (Anderson). — 5. Codeine dissolved in excess of dilute hydrochloric acid and treated with successive small quantities of *chlorate of potash*, at 70°, is converted into chlorocodeine (Anderson). — 6. Codeine dissolves in cold *oil of vitriol* without coloration (Riegel, Guy). The solution in excess of moderately strong sulphuric acid turns brown after warming for some time, and throws down amorphous codeine on addition of carbonate of soda (see above): by continued heating a green powder, corresponding with sulphonarcotide (xvi, 149) is obtained (Anderson). — 7. Strong *nitric acid* warmed with codeine acts violently on it, with formation of red vapours and a red solution, leaving on evaporation a yellow resin, the red solution of which in caustic potash yields a large quantity of methylamine when heated. — Very dilute nitric acid, at a temperature below 100°, forms nitro-codeine, which is decomposed by continued heating, with formation of a yellow resin (Anderson).

*Oil of vitriol* containing *nitric acid* immediately colours codeine palegreen, then blue-green; with traces of nitric acid, green (Couerbe). — The colourless solution in oil of vitriol is coloured a dirty brown-red by peroxide of lead, and dark-green, with brisk evolution of gas, by chromate of potash (Riegel).

8. Codeine, heated with *caustic potash solution*, solid caustic potash, or potash-lime, evolves methylamine and propylamine [or trimethylamine? (Hofmann, *Ann. Pharm.* 79, 29)], these substances being mixed with ammonia, even when the decomposition is effected at the lowest possible temperature. During the decomposition, colourless crystals, resembling benzoic acid and having an alkaline reaction, sublime in the neck of the retort; the crystals turn brown in the air, dissolve slightly in water and easily in acids, and are precipitated by chloride of platinum. If the temperature has not exceeded 175°, the alkaline residue in the retort is black-brown and decomposible by acids, with separation of humus-like flocks; it yields at a red-heat a little non-basic oil and a further quantity of volatile bases, among which ammonia predominates (Anderson). — 9. Concentrated alcoholic codeine absorbs *cyanogen*, assuming a yellow and brown colour, and deposits crystals of bicyano-codeine, the odour of cyanogen being at the same time replaced by that of hydrocyanic acid (Anderson). — 10. *Iodide of ethyl*, heated with alcoholic codeine, forms iodide of ethyl-codeine (How).

Codeine is not altered by *sesquichloride of iron* (Robiquet) or by *iodic acid* (Riegel).

*Combinations.— With Water.* A. *Bi-hydrated Codeine.*—Codeine is obtained from water, or from ether containing water, in hydrated crystals (in small white silky scales: Robiquet) which lose 6·50 p. c. (Robiquet), 5·65 p. c. (Gregory), 5·66 p. c. water (=2 at.) at 100° (Anderson). Sp. gr. = 1·3 (Hunt, *Lieb. Kopp's Jahresb.* 1855, 566). The crystals are right prismatic (trimetric, rhombic). Fig. 53, without $\alpha$, $p$ and $m$. The crystals obtained from solution in water are without the face $t$, but have in place of it a dome $z$, which would truncate the face between $t$ and $u$. $y : y = 92°\ 20'$ (Miller), $92°\ 30'$ (Kopp), $91°\ 40'$ (Sénarmont), $92°\ 8'$ (Keferstein); $u : t = 140°\ 23'$; $z : t = 157°\ 25'$; $z : t = 141°\ 37'$; $y : u = 116°\ 18'$; $y : i = 116°\ 45'$; $u : i = 126°\ 57'$ (Miller); $u : u$ over $m = 78°\ 30'$ (Kopp); $u : u$ above $= 99°\ 55'$ (Sénarmont) $= 101°\ 2'$ (Keferstein); $z : z$ above $= 134°\ 45'$ (Sénarmont) $= 134°\ 39'$ (Keferstein); $u : z = 163°\ 20'$ (Keferstein, *Pogg.* 99, 275). Cleavable parallel to $t$ (Miller, *Ann. Pharm.* 77, 381), parallel to $u$ (Kopp, *Krystallogr.* p. 266).

|  |  | | | Gerhardt. |
|---|---|---|---|---|
| 36 C | 216 | ....... | 68·14 | 67·82 |
| N | 14 | ....... | 4·41 | |
| 23 H | 23 | ....... | 7·25 | 7·46 |
| 8 O | 64 | ....... | 20·20 | |
| $C^{36}NH^{21}O^6,2HO$ | 317 | ....... | 100·00 | |

B. Codeine dissolves in cold, and more freely in hot *water*: 1,000 parts of water at 15° dissolve 12·6 parts, at 43°, 37 parts, and at 100°, 51·8 parts of codeine (Robiquet). When an excess of codeine is boiled with water, the undissolved portion melts to an oil (Robiquet).

*With Iodine.*—Iodine, triturated with codeine, forms a brown compound little soluble in water; the same body is formed also, together with iodide of codeine, by alcoholic iodine (Pelletier). Tincture of iodine throws down a scarlet-brown precipitate from hydrochlorate of codeine (v. Planta). A solution of equal parts of iodine and codeine in the smallest possible quantity of alcohol, deposits on standing small crystals which are ruby-red by transmitted, and deep violet and

diamond-like by reflected light; in a strong light they exhibit an almost metallic lustre (Anderson). Brown, crystals, having an adamantine lustre, transparent in thin laminæ, triturable to a dark orange-coloured powder, The crystals are oblique prismatic (monoclinic), with imperfect development of the faces. They exhibit two prismatic faces $u'$ and $u$ (fig. 70), only one of which, $u$, has a strongly-developed opposite face behind, the face opposite to $u'$ being wanting. To the right of $u$ are two obliquely situated prismatic faces, $d$ (above) and $d'$ (below), the opposite faces to which on the left side are wanting. The base $p$ has nearly the form of an equilateral triangle. $p : u' = 131° 5'$; $p : u = 116° 15'$; $d : d' = 77° 42'$; $p : d = 141° 29'$; the lower $p : d' = 141° 9'$; $u : u' = 147° 0'$; $d : u = 128° 0'$. The $u$ faces are curved; the others smooth and shining (Haidinger and Fötterlè. *Pogg.* 80, 554).

These crystals consist of *Teriodide of Codeine* $= C^{35}NH^{21}O^6$, 3I: hydro-sulphuric acid converts them into hydriodate of codeine, with separation of sulphur; warm oil of vitriol dissolves them with brown colour; nitric acid attacks them slowly. Boiling caustic potash takes up the iodine and leaves codeine. Nitrate of silver precipitates the greater part of the iodine. The crystals are insoluble in water and ether, but soluble with red-brown colour in alcohol (Anderson, *Edin. N. Phil. Journ.* 50, 103 : *Lieb. Kopp. Jahresb,* 1850, 429).

*With Acids.*—Codeine combines with acids, forming salts which, for the most part, are crystallisable (Robiquet). It precipitates the salts of lead, iron, cobalt, and nickel. Ammonia does not precipitate the salts of codeine (Robiquet); it does not precipitate codeine from its solution in hydrochloric acid, but throws down a part from the solution in acetic acid (Pelletier); it precipitates codeine from its salts, after some time, in small opaque crystals (Anderson). Solution of caustic potash immediately precipitates salts of codeine; a portion of the codeine, however, remains in solution in presence of a great excess of potash (Robiquet, Pelletier, Anderson). The salts of codeine are not precipitated by carbonate of soda (Anderson). They are nearly insoluble in ether (Pelletier).

*Carbonate of Codeine.* Obtained by decomposing the hydrochlorate with carbonate of silver. It is not formed on passing carbonic acid into water in which codeine is suspended, nor by precipitating salts of codeine with alkaline carbonates. — It decomposes quickly, with liberation of carbonic acid (H. How, *Chem. Gaz.* 1854, 341 ; *Lieb. Kopp.* 1854, 518).

*Phosphate of Codeine.* Phosphate of soda does not precipitate salts of codeine (v. Planta). — Aqueous phosphoric acid is neutralised with codeine, and the concentrated solution is mixed with alcohol. — Short, thick prisms, or fine scales. Easily soluble in water, from which it does not crystallise — Loses 6·27 p. c. = 3 at., water, at 100° (calc. 6·35 p. c. HO) (Anderson).

|  |  | Dried. |  |  |  | Anderson. |
|---|---|---|---|---|---|---|
| 36 C | ............................ | 216 | ........ | 54·27 | ........ | 54·25 |
| N | ............................ | 14 | ........ | 3·52 |  |  |
| 24 H | ............................ | 24 | ........ | 6·03 | ........ | 6·49 |
| 9 O | ............................ | 72 | ........ | 18·09 |  |  |
| $PO^5$ | ............................ | 71 | ........ | 18·09 |  |  |

$C^{36}NH^{21}O^6,3HO,PO^5$.... 397 ........ 100·00

*Hyposulphite of Codeine.* — Obtained in the same manner as the

morphine-salt (xvi, 430). — Rhombic prisms, containing $C^{36}NH^{21}O^6$, $HO, S^2O^2 + 5$ aq. and losing 5 at. water at 100°. Dissolves in 18 parts of cold water, and more freely in alcohol (How, *Edin. N. Phil. Journ.*, *new series*, 1, 47; *Lieb. Kopp.*, 1855, 571).

*Sulphate of Codeine.* — Four-sided prisms and tufts of needles (Anderson). Right prismatic, exhibiting the faces $y$, $m$ and $u$ of fig. 53. $y : y = 151°\ 12'$; $u : m = 113°\ 45'$. Cleavable parallel to $m$. (Miller). It is neutral only after repeated crystallisation. Dissolves in 30 parts of cold, and in a smaller quantity of hot water. — Gives off 11·3 p. c. = 5 at. water at 100° (calc. 11·45 p. c.) (Anderson).

|  |  | Dried. |  |  |  | Anderson. mean. |
|---|---|---|---|---|---|---|
| 36 C | .......................... | 216 | ........ | 62·07 | ........ | 61·54 |
| N | ........................... | 14 | ........ | 4·03 |  |  |
| 22 H | ... ........................ | 22 | ... ..... | 6·39 | ........ | 6·51 |
| 7 O | ......................... | 56 | ........ | 16·02 |  |  |
| SO³ | ........................ | 40 | ........ | 11·49 | ........ | 11·65 |
| $C^{36}NH^{21}O^6, HO, SO^3$ | .... | 348 | ........ | 100·00 |  |  |

*Iodate of Codeine.* — Formed by dissolving codeine in excess of iodic acid. Fan-shaped groups of delicate needles (Pelletier).

*Hydriodate of Codeine.* — Iodide of potassium throws down from hydrochlorate of codeine, after long standing, tufts of needles (v. Planta). — The salt is obtained by dissolving codeine in hot aqueous hydriodic acid, and cooling (Pelletier, Anderson). — Long, shining needles. Dissolves in about 60 parts of cold, and much more freely in boiling water (Anderson). The aqueous solution is not precipitated by ammonia (Pelletier): the concentrated solution is precipitated after some time (Anderson).

|  |  | at 100°. |  |  |  | Anderson. mean. |
|---|---|---|---|---|---|---|
| 36 C | ....................... ......... | 216·0 | ........ | 48·60 | ........ | 48·40 |
| N | ........................... | 14·0 | ........ | 3·15 |  |  |
| 24 H | ........................... | 24·0 | ........ | 5·40 | ........ | 5·69 |
| 8 O | ........................... ... | 64·0 | ........ | 14·45 |  |  |
| I | ................................ | 126·3 | ........ | 28·40 | ........ | 28·22 |
| $C^{36}NH^{21}O^6, HI + 2aq.$ | .... | 444·3 | ........ | 100·00 |  |  |

*Perchlorate of Codeine.* — Resembles the morphine-salt (xvi, 431), but is still more soluble in water and alcohol. Explodes when heated (Bödeker, *Ann. Pharm.* 71, 63).

*Hydrochlorate of Codeine.* — One hundred parts of codeine take up 12·76 parts (Robiquet), 12·59 parts (Regnault), 14·18 parts of hydrochloric acid gas (Gregory) (calc. = 12·2 pts.). The salt formed thereby is neutral and perfectly soluble in water (Regnault). — Hot aqueous hydrochloric acid saturated with codeine solidifies almost completely on cooling. More dilute solutions yield tufts of short needles which appear under the microscope as four-sided prisms with dihedral summits. The crystals lose 2·88 p. c. of water (= 1 at.) at 100°, and retain 3 at., which are given off, together with a little acid, at 121°, the residue having an alkaline reaction. They dissolve in 20 parts of water at 15·5°, and in less than 1 part of boiling water (Anderson). On one occasion Anderson obtained anhydrous crystals (direct from the mother-

liquor of hydrochlorate of morphine); another time the hydrated crystals were rendered anhydrous at 100°

| | *Anhydrous.* | | | Anderson. *mean.* |
|---|---|---|---|---|
| 36 C ..................................... | 216·0 | ........ | 64·38 | ........ 64·62 |
| N ..................................... | 14·0 | ........ | 4·17 | |
| 22 H ..................................... | 22·0 | ........ | 6·55 | ,,,...... 6·76 |
| 6 O ..................................... | 48·0 | ........ | 14·32 | |
| Cl ..................................... | 35·5 | ........ | 10·58 | |

$C^{36}NH^{21}O^6,HCl$  ................ 335·5  ........ 100·00

| | *Hydrated.* | | | Anderson. *mean.* |
|---|---|---|---|---|
| 36 C ..................................... | 216·0 | ........ | 59·58 | ........ 59·68 |
| N ..................................... | 14·0 | ........ | 3·86 | |
| 25 H ..................................... | 25·0 | ........ | 6·89 | ,,,...... 7·08 |
| 9 O ..................................... | 72·0 | ........ | 19·88 | |
| Cl ..................................... | 35·5 | ........ | 9·79 | |

$C^{36}NH^{21}O^6,HCl + 3aq.$ .... 362·5  ........ 100·00

Anderson (*Chem. Soc. Quart. J.* 15, 466) did not succeed in obtaining a double-salt of hydrochlorate of codeine with sal-ammoniac. (Contrary to Robiquet.)

*Nitrate of Codeine.* — Prepared by gradually adding nitric acid of sp. gr. 1·06, to powdered codeine, avoiding an excess.—Crystallises from a solution in boiling water in small prisms. Melts when heated, and solidifies to a brown resinous mass on cooling: by a stronger heat it is rapidly decomposed, and leaves a heavy, difficultly combustible charcoal (Anderson).

| | *at* 100°. | | | Anderson. |
|---|---|---|---|---|
| 36 C ................................. | 216 | ........ | 59·66 | ........ 59·40 |
| 2 N ................................. | 28 | ........ | 7·73 | |
| 22 H ................................. | 22 | ........ | 6·07 | ........ 6·54 |
| 12 O ................................. | 96 | ........ | 26·54 | |

$C^{36}NH^{21}O^6,HO,NO^5$ ...... 362  ........ 100·00

*Chromate of Codeine* forms fine yellow needles (Anderson).

Codeine-salts give bulky brown-yellow precipitates, with *phosphomolybdic* acid (xiii, 164) (Sonnenschein); and dirty-white precipitates with *phosphantimonic acid* (xiv. 277) (Schulze). — Codeine forms, with *iodide* and *bromide of mercury*, crystallisable double salts, corresponding to those of morphine, and obtained in like manner; they are soluble in hot water and alcohol (Groves). *Iodhydrargyrate of potassium* throws down, from hydrochlorate of codeine, a yellowish-white, pulverulent precipitate, which is insoluble in hydrochloric acid (v. Planta).

Codeine forms, with *mercuric chloride*, a white precipitate, which crystallises from hot water and alcohol (Anderson). Hydrochlorate of codeine is not precipitated by mercuric chloride (v. Planta).

*Terchloride of gold* forms, with hydrochlorate of codeine, a brown precipitate, soluble in hydrochloric acid (v. Planta).

*Chloroplatinate of Codeine.* — Chloride of platinum, not in excess, precipitates from moderately concentrated solutions of hydrochlorate of codeine, a pale-yellow powder, which, on standing beneath the surface of the liquid, is converted into orange-coloured crystalline granules; the mother-liquor deposits a further quantity on standing. In more

dilute solutions, the mixture remains clear at first, and afterwards deposits tufts of delicate needles having a silky lustre (Anderson). — Crystallises in fine dark-yellow, hard needles (Liebig); from a solution in hot water, in granules and as powder, with partial decomposition. By long boiling with excess of chloride of platinum it is completely decomposed. The air-dried crystals contain 4 at. water, of which 3 at. = 5·15 p. c., are given off at 100°, the remaining atom being expelled at 121°, together with a little acid, whereby the salt is rendered brown (Anderson). Dissolves in water more easily than the corresponding morphine-salt (Liebig).

|        |    | at 100°. |        |       | Anderson. mean. |
| ------ | -- | -------- | ------ | ----- | ------ |
| 36     | C  | 216·0    | ...... | 42·01 | 41·91  |
|        | N  | 14·0     | ...... | 2·72  |        |
| 23     | H  | 23·0     | ...... | 4·47  | 4·76   |
| 7      | O  | 56·0     | ...... | 10·89 |        |
|        | Pt | 98·7     | ...... | 19·19 | 19·11  |
| 3      | Cl | 106·5    | ...... | 20·72 |        |

$C^{36}NH^{21}O^6,HCl,PtCl^2$ + aq. .... 514·2 ....... 100·00

Liebig found 19·81 p. c. platinum (in the anhydrous salt?) calc. = 19·53 p. c.

*Protochloride of palladium* produces, with codeine, a yellow precipitate, which is decomposed on boiling, with separation of palladium (Anderson). — Hydrochlorate of codeine is not precipitated by *chloride of iridium and sodium* (v. Planta).

*Hydrocyanate of Codeine* is non-crystalline (Anderson).

*Hydroferrocyanate of Codeine.* Alcoholic codeine forms, with alcoholic hydroferrocyanic acid, a white precipitate which dissolves in excess of the acid, and crystallises in white needles on long standing. — Easily decomposible, and not susceptible of re-crystallization. In the dry state, or in solution, it is decomposed by heat, with evolution of a large quantity of hydrocyanic acid, and separation of white protocyanide of iron, which immediately turns blue (Dollfus).

*Ferricyanide of potassium* throws down from aqueous salts of codeine, after some time, a crystalline precipitate, a solution of which deposits a blue powder, even on evaporation in a vacuum (Dollfus).

*Hydrosulphocyanate of Codeine.* — Sulphocyanide of potassium added to acetate of codeine, occasions no precipitate at first, but in a quarter of an hour pearly crystals are produced. The crystals disappear quickly when the liquid is heated, and are again formed on cooling (O. Henry, *J. Pharm.* 24, 194). The precipitate contains hydrosulphocyanate of codeine, together with sulphocyanide of potassium, which last is not completely removed even by six or eight re-crystallisations; it is better, therefore, to prepare the salt from hydrosulphocyanic acid and codeine (Dollfus). — Stellate groups of fine transparent needles, which melt at 100° (Dollfus), and lose 2·47 p. c. = 1 at. water (Anderson).

|      |   |     |        |       | Dollfus. at 90°. |        | Anderson. at 100°. |
| ---- | - | --- | ------ | ----- | ------ | ------ | ------ |
| 38   | C | 228 | ...... | 63·68 | 62·30  | ...... | 63·20  |
| 2    | N | 28  | ...... | 7·82  |        |        |        |
| 22   | H | 22  | ...... | 6·14  | 6·13   | ...... | 6·33   |
| 6    | O | 48  | ...... | 13·43 |        |        |        |
| 2    | S | 32  | ...... | 8·93  | ...... |        | 9·04   |

$C^{36}NH^{21}O^6,C^2NHS^2$ ........ 358 ........ 100·00

The crystals contain 16·68 p. c. of hydrosulphocyanic acid (calc. = 16·52 p. c.) (Dollfus). — The salt analysed by Dollfus, dried at 90°, contains ½ at. of water (calc. 62·46 p. c. C., 5·9 H.) (Gerhardt, *N. J. Pharm.* 13, 308).

*Acetate of Codeine* is crystallisable and non-deliquescent (O. Henry).

*Oxalate of Codeine* — Crystallises from a hot solution, on cooling, in short prisms and scales, which lose 7 p. c. = 3 at. of water (calc. = 7·27 p. c.) at 100°, and turn brown at 121°, undergoing decomposition. — Dissolves in 30 parts of water at 15·5°, and in ½ pt. of water at 100° (Anderson).

| | | at 100°. | | | | Anderson. |
|---|---|---|---|---|---|---|
| 38 C | ............................ | 228 | ........ | 66·28 | ........ | 66·19 |
| N | ........ .................... | 14 | ........ | 4·07 | | |
| 22 H | ................................. | 22 | ...· ···.. | 6·39 | ........ | 6·60 |
| 10 O | ............................ | 80 | ........ | 23·26 | | |
| $C^{36}NH^{21}O^6,C^2HO^4$ | ........ | 344 | ........ | 100·00 | | |

*Tartrate of Codeine* is not crystallisable (Anderson). — *Picric acid* throws down, from hydrochlorate of codeine, a sulphur-yellow powder (v. Planta). Alcoholic picric acid scarcely precipitates an alcoholic solution of codeine (G. Kemp). — The salts of codeine are abundantly precipitated by *tincture of galls* (Robiquet). *Tannic acid* precipitates a solution containing $\frac{1}{900}$th of codeine (O. Henry, *J. Pharm.* 21, 212). Hydrochlorate of codeine behaves, towards tincture and infusion of galls, in the same manner as the morphine-salt (v. Planta).

Hydrochlorate of codeine forms, with hydrochlorate of *morphine*, a double-salt, which may be obtained according to xvi, 416. The salt contains 3 parts of codeine to 1 part of morphine (Köne, *Bull. de l'Acad. de Bruxelles*, 1837, p. 424).

C. *With Alkalis.* Codeine dissolves in aqueous *ammonia* (O. Henry), in 68·5 parts of moderately strong solution of ammonia at 15·5°, about as freely, therefore, as in water (Anderson). It does not dissolve in alkaline liquids (Robiquet). See above. It is not precipitated from a saturated aqueous solution, by concentrated solution of caustic potash (Anderson).

Codeine dissolves in *alcohol* and *ether* (Henry, Robiquet). The ethereal solution, when evaporated, yields a few crystals at first, and afterwards remains [with ether containing alcohol (Anderson)] in the form of a syrup, which crystallises only after addition of water (Robiquet).

*Oxy-iodo-azo-nucleus* $C^{30}NH^{17}I^2O^6$.

# Biniodocodeine.

$$C^{30}NH^{19}I^2O^6 = C^{36}NH^{17}I^2O^6,H^2.$$
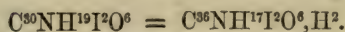
J. Brown. *Trans. Roy. Soc. Edin.* 21, 1, 49 ; *Phil. Mag.* [4] 8, 201 ; *Ann. Pharm.* 92, 325 ; *J. pr. Chem.* 63, 370 ; *Pharm. Centr.* 1854, 797 ; *Lieb. Kopp's Jahresb.* 1854, 510.

Aqueous chloride of iodine (obtained by passing chlorine into water

in which iodine is suspended till nearly the whole is dissolved) throws down from concentrated aqueous solutions of hydrochlorate of codeine a yellow crystalline precipitate, which is deposited from a hot, moderately dilute alcoholic solution, on cooling, in stellate crystals.

The crystals contain iodine (hydriodate of biniodocodeine, or biniodo-codeine? Kr.). They lose a portion of their iodine on re-crystallisation from alcohol, and separate again from a concentrated alcoholic solution, in an amorphous mass. They are insoluble in water, but soluble in cold hydrochloric acid, from which they separate on heating, in the form of an oil, afterwards solidifying to a flocculent mass. They are precipitated from the solution in hydrochloric acid by potash and ammonia. — Bichloride of platinum, added to the solution in hydrochloric acid, forms a yellow precipitate containing 12·20 p. c. platinum, and corresponding to the formula $C^{35}NH^{19}I^2O^6$, $HCl,PtCl^2 + 2HO$ (calc. 11·95 p. c. Pt.).

*Oxy-bromo-azo-nucleus* $C^{36}NH^{16}BrO^6$.

## Bromocodeine.

$$C^{36}NH^{20}BrO^6 = C^{36}NH^{16}BrO^6,H^2.$$
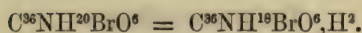
ANDERSON. *Ann. Pharm.* 77, 362.

*Preparation.* Bromine-water is added by small portions to finely powdered codeine till the whole is dissolved (small crystals of hydrobromate of bromocodeine being deposited when saturated bromine-water is used). The bromocodeine thereby formed is at once precipitated by ammonia as a silver-white powder, and freed from codeine thrown down at the same time by solution in hydrochloric acid, precipitation by ammonia, and re-crystallisation from alcohol. It is apt to retain small quantities of codeine.

*Properties.* The hydrated crystals lose their water at 100°. Melts to a colourless liquid when heated.

|       |       | at 100°. |       |        |       | Anderson. |
|-------|-------|----------|-------|--------|-------|-----------|
| 36 C  | ..... | 216      | ..... | 57·14  | ..... | 57·21     |
| N     | ..... | 14       | ..... | 3·70   |       |           |
| 20 H  | ..... | 20       | ..... | 5·29   | ..... | 5·44      |
| Br    | ..... | 80       | ..... | 21·16  | ..... | 21·50     |
| 6 O   | ..... | 48       | ..... | 12·71  |       |           |
| $C^{36}NH^{20}BrO^6$ | ..... | 378 | ..... | 100·00 | | |

Decomposes a little above its melting point. — A solution in *oil of vitriol* assumes a dark colour on heating. — Less easily decomposed than codeine by *nitric acid.* — An excess of *bromine* gradually converts it into hydrobromate of tribromocodeine, which is precipitated.

Crystallised bromocodeine forms prisms with dihedral summits, or small shining needles containing sometimes 2·32 p. c. (= 1 at.), sometimes 6·66 p. c. (= 3 at.) of water.

*Hydrobromate of Bromocodeine.* — Small prisms, slightly soluble in

cold, very easily soluble in hot water. Does not lose its water of crystallisation at 100°.

| | | at 100°. | | | | Anderson. |
|---|---|---|---|---|---|---|
| 36 | C | 216 | ........ | 45·28 | ........ | 45·18 |
| | N | 14 | ........ | 2·93 | | |
| 2 | Br | 160 | ........ | 33·54 | | |
| 23 | H | 23 | ........ | 4·84 | ........ | 5·25 |
| 8 | O | 64 | ........ | 13·41 | | |
| C$^{36}$NH$^{20}$BrO$^6$HBr + 2 aq. | | 477 | ........ | 100·00 | | |

*Hydrochlorate of Bromocodeine* forms star-shaped groups of needles, resembling those of hydrochlorate of codeine. — *Chloro-platinate of Bromocodeine* is a pale-yellow powder, insoluble in water and alcohol, containing 16·98 p. c. platinum (calc. 16·89 p.c. Pt.).

Bromocodeine dissolves easily in *alcohol*, especially when hot. It is nearly insoluble in *ether*.

### *Oxy-bromo-azo-nucleus* C$^{36}$NH$^{16}$Br$^3$O$^6$.

### Terbromocodeine.

$$C^{36}NBr^3H^{18}O^6 = C^{36}NBr^3H^{16}O^6,H^2.$$
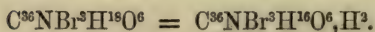
ANDERSON. *Ann. Pharm.* 77, 365.

Codeine is converted by bromine-water into hydrobromate of bromo-codeine, and more bromine-water is then added till a fresh addition no longer produces a bright-yellow precipitate on standing for a day. The precipitated hydrobromate of terbromocodeine is collected, washed with water, dissolved in hydrochloric acid, and precipitated by ammonia. To purify the flocculent precipitate of terbromocodeine thus obtained, it is washed with water, dissolved in alcohol, and precipitated by water, then again dissolved in alcohol, and thrown down by ether.

White, heavy, amorphous precipitate, grey after drying.

| | | at 100°. | | | | Anderson. |
|---|---|---|---|---|---|---|
| 36 | C | 216 | ........ | 40·27 | ........ | 39·69 |
| | N | 14 | ........ | 2·61 | | |
| 3 | Br | 240 | ........ | 44·77 | ........ | 44·68 |
| 18 | H | 18 | ........ | 3·35 | ........ | 3·66 |
| 6 | O | 48 | ........ | 9·00 | | |
| C$^{26}$NH$^{18}$Br$^3$O$^6$ | | 536 | ........ | 100·00 | | |

Turns brown on *heating*, and undergoes decomposition when melted, leaving a difficultly combustible charcoal.

Insoluble in *water*. — Behaves as a feeble base, and forms amorphous sparingly soluble salts.

*Hydrobromate of Terbromocodeine.*—Bright yellow, amorphous powder, slightly soluble in cold, and rather more soluble in hot water.

|  |  | at 100°. |  |  | Anderson. mean. |
|---|---|---|---|---|---|
| 72 | C ................................... | 432 | ........ | 32·84 | ........ 32·21 |
| 2 | N ................................... | 28 | ........ | 2·12 | |
| 9 | Br ................................. | 720 | ........ | 54·75 | .......... 55·03 |
| 39 | H ................................... | 39 | ........ | 2·96 | .......... 2·85 |
| 12 | O ................................... | 96 | ........ | 7·33 | |

| 2C³⁶NBr³H¹⁸O⁶,3HBr ......... | 1315 | ....... | 100·00 |
|---|---|---|---|

*Hydrochlorate of Terbromocodeine.*—Deposited from a solution of terbromocodeine in hot dilute hydrochloric acid, on cooling, as an amorphous powder.

*Chloro-platinate of Tribromocodeine.* — Brown-yellow powder, soluble in water and alcohol. Contains, at 100°, 13·07 p. c. platinum, agreeing, therefore, with the formula $C^{36}NBr^3H^{18}O^6,HCl,PtCl^2$ (calc. 13·29 p. c. Pt.).

Terbromocodeine is easily soluble in *alcohol,* insoluble in ether.

*Oxy-chloro-azo-nucleus* $C^{36}NH^{18}ClO^6$.

## Chlorocodeine.

$$C^{36}NH^{20}ClO^6 = C^{36}NH^{18}ClO^6,H^2.$$
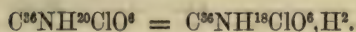
ANDERSON. *Ann. Pharm.* 77, 368.

Finely powdered chlorate of potash is added by degrees to a solution of codeine in excess of dilute hydrochloric acid, at 60° or 70°, so long as the precipitate produced by ammonia in a test-portion of the liquid continues to increase. The liquid is then precipitated with a slight excess of ammonia, and the silvery, crystalline precipitate is dissolved in hydrochloric acid, treated with animal charcoal, again precipitated by ammonia, and allowed to crystallise from hot alcohol. If the action of chlorate of potash were continued too long, decomposition-products would be formed. Some decomposition always takes place, and hence the filtrate from the chlorocodeine is coloured dark-red.

The crystals obtained from water are hydrated chlorocodeine. They are rendered anhydrous by drying at 100°.

|  |  | at 100°. |  |  | Anderson. mean. |
|---|---|---|---|---|---|
| 36 | C...................... | 216 | ........ | 64·76 | ........ 64·81 |
| | N...................... | 14 | ........ | 4·19 | |
| | Cl ..................... | 35·5 | ........ | 10·64 | ........ 10·32 |
| 20 | H ..................... | 20 | ........ | 5·99 | ........ 6·15 |
| 6 | O ..................... | 48 | ........ | 14·42 | |

| C³⁶NH²⁰ClO⁶ ........ | 333·5 | ........ | 100·00 |
|---|---|---|---|

Chlorocodeine treated with boiling *nitric acid,* is less easily decomposed than codeine, evolving red vapours and a peculiar gas having a very penetrating odour. — Dissolves in cold, and blackens in hot *oil of vitriol.*

*Hydrated Chlorocodeine.* — Obtained from hot aqueous solutions of

small prisms, closely resembling, and probably isomorphous with those of bromocodeine. — Loses 7·36 p. c. (= 3 at.) of water at 100° (calc. 7·48 p. c. HO).

Dissolves very slightly in hot water. — The salts of chlorocodeine resemble those of bromocodeine.

*Sulphate of Chlorocodeine.* — Radiated groups of short prisms, easily soluble in hot water and alcohol.

|  | | *Crystals.* | | | | *Anderson.* |
|---|---|---|---|---|---|---|
| $C^{36}NH^{20}ClO^6$ | ............... ........ | 333·5 | ........ | 79·63 | | |
| $SO^3,HO$ | ............................ | 49 | ........ | 11·75 | ........ | 11·90 |
| 4 HO | ............................ | 36 | ........ | 8·62 | ........ | 8·76 |
| $C^{36}NH^{20}ClO^6,SO^3,HO + 4aq.$ | .... | 418·5 | ........ | 100·00 | | |

*Chloroplatinate of Chlorocodeine.* — Hydrochlorate of chlorocodeine forms, with bichloride of platinum, a pale-yellow precipitate but slightly soluble in water.

|  | | *at* 100°. | | | | *Anderson.* |
|---|---|---|---|---|---|---|
| 36 C | ............................ | 216 | ........ | 40·02 | ........ | 40·30 |
| N | ............................ | 14 | ...... | 2·59 | ........ | |
| 21 H | ............................ | 21 | ........ | 3·89 | ........ | 4·09 |
| 6 O | ............................ | 48 | ........ | 8·91 | | |
| Pt | ............................ | 98·7 | ........ | 18·28 | ........ | 18·29 |
| 4 Cl | ............................ | 142 | ........ | 26·31 | | |
| $C^{36}NH^{20}ClO^6,HCl,PtCl^2$ | .... | 539·7 | ........ | 1000·00 | | |

Chlorocodeine dissolves easily in strong *alcohol*, especially when hot. It is only slightly soluble in ether.

*Oxy-nitro-azo-nucleus* C³⁶NH¹⁸XO⁶.

# Nitrocodeine.

$$C^{36}N^2H^{20}O^{10} = C^{36}NH^{18}XO^6,H^2.$$
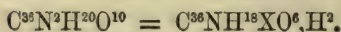
ANDERSON. *Ann. Pharm.* 77, 358; Prelim. Notice *Ann. Pharm.* 75, 80.

*Preparation.* (See p. 30.) Finely powdered codeine is added to moderately hot (not boiling) nitric acid of sp. gr. 1·06, and the liquid is heated for a few minutes, or until a small portion gives an abundant precipitate, on addition of ammonia. The whole is then neutralized with ammonia, which throws down nitrocodeine in silvery laminæ. The precipitate is dissolved in hydrochloric acid, boiled with animal charcoal, precipitated several times by ammonia to remove resin and unchanged codeine, and crystallised from dilute alcohol or ether-alcohol. — Careful treatment is necessary to prevent the decomposition of the nitrocodeine by nitric acid. The decomposition is manifested by the evolution of red vapours, and by the red colour of the liquid which has been precipitated by ammonia.

*Properties.* Yellow or fawn-coloured silky, delicate needles appearing under the microscope as four-sided prisms with dihedral

summits. — Melts, when cautiously heated, to a yellow oil, which solidifies in the crystalline state.

|  |  | Crystals. |  |  |  | Anderson. mean. |
|---|---|---|---|---|---|---|
| 36 | C | ............ .... | 216 | ........ | 62·79 | ........ 62·66 |
| 2 | N | .............. | 28 | ........ | 8·11 |  |
| 20 | H | ................ | 20 | ........ | 5·81 | ........ 5·85 |
| 10 | O | .... .......... | 80 | ........ | 23·29 |  |
|  | $C^{36}NH^{20}XO^6$ | .... | 344 | ........ | 100·00 |  |

*Decompositions.* Nitrocodeine, when strongly *heated*, explodes without flame, leaving a heavy charcoal. — On warming it with *hydrosulphate of ammonia*, sulphur is precipitated, and a brown filtrate is obtained, from which ammonia throws down a brown, amorphous precipitate. This precipitate, when dissolved in hydrochloric acid, boiled with animal charcoal, and precipitated by ammonia, yields a pale-yellow base, easily soluble in alcohol, from which it is usually deposited in the form of an amorphous powder, but was obtained on one occasion in brown crystals: probably *Azocodeine* $C^{36}N^2H^{20}O^6$.

*Combinations.* Nitrocodeine dissolves slightly in hot *water*, crystallising on cooling. — It forms, with *acids*, neutral soluble salts, from which ammonia and potash precipitate the nitrocodeine as a crystalline powder.

*Sulphate of Nitrocodeine* forms tufts of neutral needles, very soluble in hot water. The salt, dried at 100°, contains 10·13 p. c. sulphuric acid, corresponding to the formula $C^{36}NH^{20}XO^6,SO^3,HO$ (calc. 10·17 p. c. $SO^3$).

*Hydrochlorate of Nitrocodeine.* — Nitrocodeine dissolves readily in hydrochloric acid, and yields this salt in the form of a resinous mass on evaporation.

*Chloroplatinate of Nitrocodeine.* — Hydrochlorate of nitrocodeine throws down from bichloride of platinum a yellow powder insoluble in water and in alcohol. The air-dried powder loses 6·56 p. c. of water = 4 at., at 100° (calc. = 6·14 p. c. HO).

|  |  | at 100°. |  |  |  | Anderson. |
|---|---|---|---|---|---|---|
| 36 | C | ................................ | 216 | ........ | 39·25 | ........ 39·11 |
| 2 | N | ................................ | 28 | ........ | 5·08 |  |
| 21 | H | ................................ | 21 | ........ | 3·81 | ........ 4·09 |
| 10 | O | ................................ | 80 | ........ | 14·58 |  |
|  | Pt | ................................ | 98·7 | ........ | 17·93 | ........ 17·88 |
| 3 | Cl | ................................ | 106·5 | ........ | 19·35 |  |
|  | $C^{36}NH^{20}XO^6,HCl,PtCl^2$ | .... | 550·2 | ........ | 100·00 |  |

The *oxalate* forms fine yellow short prisms, easily soluble in water.

Nitrocodeine dissolves freely in hot *alcohol*, slightly in *ether*.

*Conjugated Compounds of Codeine.*

## Bicyanocodeine.

$$C^{40}N^3H^{21}O^6 = C^{38}Cy^2AdH^{17}O^6,H^2.$$
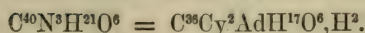
ANDERSON. *Ann. Pharm.* 77, 371.

Cyanogen gas is slowly passed into a saturated solution of codeine in alcohol, and the crystals thereby formed are collected on a filter. On again treating the filtrate with cyanogen, a further quantity of less pure crystals is obtained. The crystals are dissolved in warm ether-alcohol, through which cyanogen is passed to convert any unchanged codeine, and the colourless or yellowish crystals which form on cooling are purified by re-crystallisation from hot alcohol or ether-alcohol.

Highly-lustrous, thin, six-sided laminæ. Contains no water of crystallisation.

|  |  | *In vacuo.* |  |  |  | Anderson. |
|---|---|---|---|---|---|---|
| 40 | C | 240 | | 68·37 | | 68·13 |
| 3 | N | 42 | | 11·68 | | 11·66 |
| 21 | H | 21 | | 5·97 | | 6·05 |
| 6 | O | 48 | | 13·97 | | 14·16 |
| $C^{40}N^3H^{21}O^6$ | | 351 | | 100·00 | | 100·00 |

Bicyanocodeine dissolves with difficulty in *water*, more easily on addition of *alcohol*. The aqueous solution deposits crystals of codeine on evaporation. With *hydrochloric, sulphuric,* and *oxalic acids* it forms difficultly soluble crystalline compounds, which, when kept for 24 hours, evolve an odour of hydrocyanic acid, and, even before that, yield ammonia on addition of potash. *Bichloride of platinum* added to the solution in hydrochloric acid produces an immediate evolution of hydrocyanic acid.

## Ethyl-codeine.

$$C^{40}NH^{25}O^6 = C^{36}N(C^4H^5)H^{18}O^6,H^2.$$
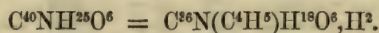
H. How. *Chem. Soc. Qu. J.* 6, 125; *Ann. Pharm.* 88, 339.

*Vinecodeïn.*

A mixture of finely-powdered codeine with iodide of ethyl and a quantity of absolute alcohol sufficient to dissolve the codeine, heated in a water-bath for two hours in a sealed tube, solidifies, from formation of crystals of hydriodate of ethylcodeine. The crystals are collected, washed with alcohol, and re-crystallised from water.

An aqueous solution of these crystals decomposed by oxide of silver yields *hydrated ethylcodeine* having a strong alkaline reaction; it absorbs carbonic acid on evaporation, and leaves a coloured translucent residue. This residue is decomposed by heating with

iodide of ethyl, in the same manner as methyl-morphine (xvi., 439) is decomposed when heated with iodide of methyl, without formation of biethylcodeine.

*Hydriodate of Ethylcodeine* forms tufts of white needles. Its aqueous solution is not precipitated by ammonia or potash, but becomes turbid on boiling with solution of caustic potash, apparently from decomposition of the ethylcodeine.—Dissolves easily in cold water.

|    |   |      | at 100° |        |       |        | How. |
|----|---|------|---------|--------|-------|--------|------|
| 40 | C | .... | 240     | ...... | 52·73 | ...... | 52·59 |
|    | N | .... | 14      | ...... | 3·07  |        |      |
| 26 | H | .... | 26      | ...... | 5·71  | ...... | 5·87 |
| 6  | O | .... | 48      | ...... | 10·57 |        |      |
|    | I | .... | 127     | ...... | 27·92 | ...... | 27·91 |
| $C^{36}N(C^4H^5)H^{20}O^6,HI$ | | .... | 455 | ...... | 100·00 | | |

*Primary Nucleus* $C^{36}H^{28}$.

## Sycocerylic Alcohol.

$$C^{36}H^{30}O^2 = C^{36}H^{28},H^2O^2.$$
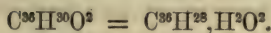
W. De la Rue and H. Müller. *Lond. Roy. Soc. Proc.* 10, 298; *Phil. Mag.* [4] 20, 225; *Ann. Pharm.* 116, 255; *Zeitschr. Ch. Pharm.* 3, 743; *Rép. Chim. pure*, 2, 410;—*Phil. Trans.* 1860, 43; *Chem. Soc. Qu. J.* 15, 62; *J. pr. Chem.* 89, 221; *Chem. Centr.* 1862, 705; *Kopp's Jahresb.* 1861, 637.

*Source.* Occurs as acetate of sycoceryl, in the resin of *Ficus rubiginosa*, from New South Wales.

*Preparation.* The resin is first treated with cold alcohol to remove sycoretin, and the residue is exhausted with boiling alcohol; the solution, on cooling, yields crystals of acetate of sycoceryl, a small quantity of another flocculent substance being also deposited towards the end of the crystallisation. When the solution is allowed to cool only to about 40°, and the crystals then formed are separated, recrystallised from alcohol, and afterwards treated, at 30°, with a quantity of ether insufficient for complete solution, the acetate is obtained, whilst a neutral crystalline body (containing 75·56 p. c. C, and 12·3 H), insoluble in ether, is left behind. The acetate is decomposed by boiling with sodium-alcohol, and the sycocerylic alcohol thereby formed is thrown down by addition of water, and crystallised from alcohol.

*Properties.* Very thin crystals, resembling caffeine, usually aggregated in masses like Wavellite. Melts at 90° to a liquid heavier than water, and solidifies in the crystalline state on cooling; after being strongly heated it solidifies to a transparent glass, which becomes crystalline in contact with alcohol. Distils partly undecomposed.

|  |  |  |  |  |  | De la Rue and Müller. |
|  |  |  |  |  |  | *mean.* |
| 36 C............. | 216 | ........ | 82·44 | ........ | 82·39 |
| 30 H | ........ | 30 | ........ | 11·45 | ........ | 11·38 |
| 2 O | ........ | 16 | ... .... | 6·11 | ... .... | 6·23 |
| $C^{36}H^{30}O^2$ | .... | 262 | ........ | 100·00 | ........ | 100.00 |

Homologous with benzylic alcohol (xii, 18) and cuminic alcohol (xiv, 14).

*Decompositions.* 1. Sycocerylic alcohol is only slowly attacked on boiling with dilute *nitric acid:* the dark-yellow resin formed after six hours, when washed and dried and afterwards dissolved in warm alcohol, yields white and yellow crystals, easily soluble in aqueous ammonia and potash, and precipitable by alcoholic neutral acetate of lead, probably a mixture of *sycocerylic acid,* $C^{36}H^{18}O^4$, and nitrosycocerylic acid. — 2. Moderately dilute aqueous *chromic acid,* boiled with sycocerylic alcohol for eight hours, produces no sycocerylic acid : on one occasion, neutral thin prisms, probably of sycocerylic aldehyde, $C^{36}H^{28}O^2$, were produced. — 3. The alcohol dissolves easily in *oil of vitriol,* forming a brown solution from which water throws down a viscid resin ; no conjugated compound of sulphuric acid remains in solution. — 4. Sycocerylic alcohol is readily attacked by *chlorine* and *bromine,* and forms yellow crystals with *iodine.* — 5. A solution of sycocerylic alcohol in benzene evolves hydrochloric acid gas when treated with *pentachloride of phosphorus* at 60°. If, after the evolution of gas has ceased, the remaining chloride of phosphorus is removed, and the benzene solution is washed with water and aqueous alkali and evaporated, there remains an amorphous, greenish, viscid residue, easily soluble in ether and chloroform, but difficultly soluble in alcohol. On one occasion crystals were also obtained. — 6. *Potassium* evolves hydrogen from melted sycocerylic alcohol, and becomes covered with a white crust, which, when heated till it melts, blackens and takes fire. — 7. Sycocerylic alcohol, treated with fused *caustic potash,* evolves hydrogen without forming sycocerylic acid. — 8. With *chloride of acetyl* it forms acetate of sycoceryl, and with *chloride of benzoyl,* benzoate of sycoceryl.

*Combinations.* Sycocerylic alcohol is insoluble in *water,* aqueous *ammonia,* and *alkalis.* It dissolves readily in *alcohol:* a hot saturated solution forms a semi-solid mass of crystals on cooling ; a solution in very dilute alcohol deposits, on cooling, a jelly, which afterwards becomes crystalline. — Dissolves in *ether, benzene, chloroform,* and *light mineral oil.*

## Acetate of Sycoceryl.

$$C^{40}H^{32}O^4 = C^{36}H^{29}O,C^4H^3O^3.$$
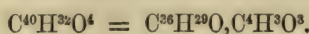
Warren de la Rue & Müller.

*Sycocerylic Acetate.* — *Sycoceryl-acetic ether.* — *Essigsycocerylester.* A constituent of the resin of *Ficus rubiginosa,* from which it is obtained by the process already described (p. 43).

On gently warming sycocerylic alcohol with chloride of acetyl, a large quantity of hydrochloric acid gas is evolved, and a solution is obtained which, when boiled with water to remove excess of the chloride, solidifies to crystals of acetate of sycoceryl. The crystals are purified by re-crystallisation from alcohol.

*Properties.* Crystallises from alcohol, in thin laminæ resembling cholesterin, and from ether in flat six-sided tables. Melts at 118—120°, and solidifies only below 80° to a mass which is transparent at first, but afterwards becomes opaque and crystalline. Distils unchanged; when it is too strongly heated the distillate smells rancid and like acetic acid. Brittle; strongly electric when rubbed. Neutral.

|  |  |  |  |  |  | De la Rue and Müller. mean. |
|---|---|---|---|---|---|---|
| 40 C | .................. | 240 | ........ | 78·94 | ........ | 79·09 |
| 32 H | .................. | 32 | ........ | 10·52 | ........ | 10·28 |
| 4 O | .................. | 32 | ........ | 10·53 | ........ | 10·63 |
| $C^{36}H^{29}O,C^{4}H^{3}O^{3}$ .... | | 304 | ........ | 100·00 | ........ | 100·00 |

Hot dilute *nitric acid* converts it into a resin. The easily prepared solution in fuming nitric acid is precipitated by water in amorphous yellow flocks. — Dissolves easily and without coloration in *oil of vitriol;* the solution becomes brown on standing, and gives off traces of sulphurous and acetic acids; water precipitates from the solution a hard substance, fusible below 100°, difficultly soluble in alcohol, easily soluble in chloroform and benzene. — Acetate of sycoceryl forms resinous compounds with *chlorine, bromine,* and *iodine;* the last two when added gradually to a warm alcoholic solution of the acetate, form crystals of a colourless bromine- or iodine-compound, which are deposited on cooling. — Acetate of sycoceryl is not affected by boiling solution of *caustic potash,* but is decomposed by the fused hydrate, with liberation of hydrogen. *Sodium-alcohol* decomposes it, even at 30°, forming acetic acid and sycocerylic alcohol.

Acetate of sycoceryl dissolves very easily in hot *alcohol,* and in *acetic acid, acetone, chloroform, ether, benzene,* and *oil of turpentine.* It is not precipitated by alcoholic *neutral acetate of lead,* or by alcoholic *acetate of copper.*

## Benzoate of Sycoceryl.

$$C^{50}H^{34}O^4 = C^{36}H^{29}O,C^{14}H^5O^3.$$
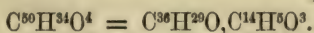
WARREN DE LA RUE & MÜLLER. *Loc. cit.*

Sycocerylic alcohol is dissolved in chloride of benzoyl (no gas being evolved in the cold), and the solution is heated as long as hydrochloric acid gas is given off. The crystalline mass formed on cooling is thrown into a warm aqueous solution of bicarbonate of potash, with which it is warmed for several hours. The resin thereby separated, after washing with warm water and boiling alcohol, is dissolved in boiling ether, from which it is obtained in crystals. Boiling absolute alcohol dissolves only a trace of the crystalline substance and deposits

it again, on cooling, in small crystals recognisable under the micro-
scope. It dissolves with difficulty in cold ether, and in all propor-
tions in chloroform and benzene, crystallising in prisms on evaporation.
Sodium-alcohol decomposes it only on long boiling, with formation of
sycocerylic alcohol and benzoate of soda.

## Sycoretin.

The resin of *Ficus rubiginosa* is resolved by treatment with alcohol
into about 73 per cent. of sycoretin, soluble in the cold, 14 p. c. of
acetate of sycoceryl soluble in hot alcohol, and 13 p. c. of residue,
consisting of caoutchouc, sand, and fragments of bark.

On mixing the neutral pale-brown solution in cold alcohol with
water, the sycoretin is precipitated, and may be rendered colourless
by repeated solution and precipitation. A saturated alcoholic solu-
tion deposits, in the cold, a small quantity of a crystalline substance,
sycoretin in a purer state remaining in solution. The latter may be
separated, by fractional precipitation with water, into two portions,
the first of which contains 74·65 p. c. C. and 10·11 H., the second
77·89 p. c. C and 9·94 H.

Sycoretin is amorphous, white, neutral, very brittle and extremely
electric. It melts in boiling water to a thick liquid which floats on
the surface. Melts alone at 100°.

Sycoretin undergoes decomposition a few degrees above its
melting-point, frothing up and giving off water with a wax-like
odour. When further heated it melts quietly, and yields a distillate
containing acetic acid and tar, charcoal being left behind. — It is
attacked by *nitric acid* and dissolved on boiling therewith; water
precipitates from the yellow solution a slightly acid nitro-compound
which is soluble with dark colour in aqueous alkalis, and forms an
explosive compound with potash. In this reaction a little oxalic acid
is formed, but no picric acid. — Sycoretin dissolves in *oil of vitriol*
with fine green colour, without forming sugar; water throws down
from the solution a brown precipitate less soluble than sycoretin. —
*caustic potash* acts on sycoretin in the same way as oil of vitriol.

Sycoretin is insoluble in *water*, dilute *acids*, *ammonia*, and aqueous
*alkalis*. It is not precipitated from its alcoholic solution by *neutral
acetate of lead* or *acetate of copper*. — Dissolves easily in *alcohol*, *ether*,
*chloroform*, and *oil of turpentine* (Warren de la Rue & Müller).

## Axinic Acid.

$$? \ C^{36}H^{28}O^4 \ = \ C^{36}H^{28}?O^4.$$
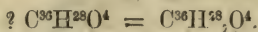
F. Hoppe. *J. pr. Chem.*, 80, 130.

*Source.* Occurs as glyceride (triaxin) in the *Age* or *Axin* of the
Mexicans (p. 47).

When axin is exhausted with ether, the ether evaporated, and
the residue saponified with alcoholic potash, the alkaline solution, on
cooling, deposits of laurate potash, which must be removed by filtra-

tion. The filtrate mixed with hydrochloric acid and water, deposits a thick brown oil, which is to be washed with dilute alcohol by decantation, dissolved in ether, recovered from the solution by distillation, and dried over a water-bath. It does not solidify at $0°$, and is insoluble in water but soluble in cold, and more easily in hot, alcohol and ether. It possesses these properties and the following composition, however, only when exposure to air has been avoided throughout the process of preparation.

| | | | | | | F. Hoppe. | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *a.* | | *b.* | | *c.* |
| 36 C | 216 | .... | 78·25 | .... | 77·78 | .... | 77·48 | .... | 76·86 |
| 28 H | 28 | .... | 10·14 | .... | 10·44 | .... | 10·31 | .... | 10·25 |
| 4 O | 32 | .... | 11·61 | .... | 11·78 | .... | 12·21 | .... | 12·89 |
| $C^{36}H^{28}O^4$ | 276 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 |

*b* and *c* had probably taken up a little oxygen on opening the tube (Hoppe).

*Decompositions.* A drop of axinic acid exposed to the air takes up oxygen, and becomes covered with a pellicle in one or two minutes. The acid prepared with partial access of air solidifies above $0°$, smells like linseed-oil varnish, and has the composition of linoleic acid (xvi, 305). Left in contact with oxygen for twelve hours, the acid solidifies completely ; exposed to the air for some days, and frequently moistened with ether to ensure the contact of air, notwithstanding the crust, it increases about 13·7 p. c. in weight. By this oxidation, there are formed 58·8 p. c. of aginin, insoluble in ether, and 54·9 p. c. physetoleic acid (xvi, 317).

*Aginin,* purified as far as possible by ether, is a bright-yellow, amorphous, friable substance, not fusible without decomposition, and very hygroscopic. It contains, after drying in a vacuum, 58·35 to 60·31 p. c. C., and 6·70 to 7·51 H. : aginin formed by the action of the air on axin, exhibits the same composition. — When heated to $80°$, it is decomposed, with evolution of water-vapour and colourless gases, which are absorbed by caustic potash. Heated to $110°$ with water in a sealed tube, it forms a dark-brown solution, with dark flocks. It dissolves in nitric acid, with evolution of nitric oxide, and water throws down colourless needles from the solution. Aginin dissolves in caustic alkalis, forming brown solutions, which are precipitated by acids in flocks.

*Age or Axin.* Obtained in Mexico by boiling a species of coccus (*Coccus Axin*) with water. — Dark-yellow, buttery ; hardens on exposure to the air. Has an agreeable odour, like that of arnica flowers. Dissolves with difficulty in cold, more easily in hot alcohol, and very easily in ether, leaving a hardened crust of aginin. The ethereal solution leaves, when evaporated, a brown fat, which melts at $31°$, and contains, on the average, 78·03 p. c. C., 10·34 H., and 11·63 O. It is composed of laurostearin (with a little palmitin) and triaxin, and on account of this latter constituent, rapidly absorbs oxygen from the air, forming thereby aginin, and a glyceride of physetoleic acid (xvi, 317) (Hoppe, *J. pr. Chem.* 80, 102).

*Oxygen-nucleus* $C^{36}H^{18}O^{10}$.

# Usnic Acid.

? $C^{36}H^{18}O^{14} = C^{36}H^{18}O^{10},O^4$.
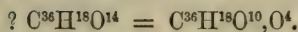
W. KNOP. *Ann. Pharm.*, 49, 103 ; *J. pr. Chem.*, 31, 196.
ROCHLEDER & HELDT. *Ann. Pharm.*, 48, 9.
KNOP & SCHNEDERMANN. *J. pr. Chem.*, 39, 363.
STENHOUSE. *Phil. Trans.*, 1848, 88 ; *Ann. Pharm.*, 68, 97, and 104.
HESSE. *Ann. Pharm.*, 117, 343.

*Usneïn. Alpha-usninsäure* (Hesse). — Thomson's *Parietin* (xvi, 171), which Gerhardt regarded as usnic acid (*Traité*, 3, 789), appears to be impure chryso-phanic acid.

*Sources.* Usnic acid occurs in the following lichens : *Usnea florida, U. hirta, U. plicata* (Knop); *Usnea barbata* (Rochleder & Heldt); *Cladonia digitata, Cl. bellidiflora, Cl. maculata, Cl. rangiferina, Cl. uncinata, Lecidea geographica, Biatora lucida, Parmelia hæmatomma, P. sarmentosa* (Knop); *P. furfuracea* (Rochleder & Heldt); *P. saxatilis* (Overbeck, *N. Br. Arch.* 82, 150); *Lecanora ventosa* (Knop); *Ramalina calicaris* (Rochleder & Heldt). *Evernia prunastri* contains usnic and also evernic acid (Stenhouse).

*Preparation.* Best from *Cladonia rangiferina* or *Usnea florida* (Stenhouse). 1. The comminuted lichen is softened in water, and exhausted with thin milk of lime : from the dark-yellow solution thus obtained, the usnic acid is precipitated by hydrochloric or acetic acid, and the precipitate is dried and purified by crystallisation from alcohol, with aid of animal charcoal (Stenhouse). Hesse boils the liquid (acidified with hydrochloric acid) for some time, whereby the usnic acid is thrown down in the crystalline state : he then washes the precipitate with water, boils it with alcohol to remove resin, and purifies it by crystallisation from hot acetic acid, with the aid of charcoal. — 2. The chopped lichen is digested with ether for several days ; the ether is distilled from the extract, and the residue mixed with alcohol ; the usnic acid is then separated in crystals, which may be purified by washing with hot alcohol (Knop). — 3. Rochleder & Heldt exhaust with ammoniacal alcohol, precipitate with acetic acid, and purify by re-crystallisation.

Hesse's *beta-usnic* acid is obtained from *Cladonia rangiferina*. The lichen is washed with luke-warm water and exhausted with dilute caustic soda ; the alkaline solution is precipitated by hydrochloric acid, and the precipitate is washed, dried, and exhausted with ether. After distilling off the ether, the residue is mixed with alcohol, which takes up resin and leaves beta-usnic acid. The latter is purified by crystallisation from strong boiling alcohol, with the help of animal charcoal. Beta-usnic acid exhibits the characters of usnic acid, with the exception of its melting-point, which is 175°. It yields, when heated, a sublimate of white laminæ and flat needles, and contains 62·7 p. c. C., and 5·3 H. (Hesse).

*Properties.* Pure sulphur-yellow, transparent prisms, triturable to a paler, strongly electric powder (Knop). Delicate, interlaced, shining, pale-yellow needles (Rochleder & Heldt). Straw-yellow, shining

laminæ (Stenhouse). Melts at 203° (Hesse), 200° (Knop), to a yellow transparent resin, which forms a crystalline solid on cooling. — Taste · less (Rochleder & Heldt).

<p style="text-align:center"><em>Calculations.</em></p>

| According to Hesse. | | According to Strecker. | | According to Gerhardt. | |
|---|---|---|---|---|---|
| 36 C............ | 62·42 | 38 C .. ... .... | 63·7 | 38 C......... .... | 64·04 |
| 18 H ........ | 5·20 | 18 H...... .... | 5·0 | 16 H......... .... | 4·49 |
| 14 O ........ | 32·38 | 14 O.. ... .... | 31·3 | 14 O........ .... | 31·47 |
| $C^{36}H^{18}O^{14}$ .... | 100·00 | $C^{38}H^{18}O^{14}$ .... | 100·0 | $C^{38}H^{16}O^{14}$ .... | 100·00 |

<p style="text-align:center"><em>Analyses.</em></p>

| | a. Rochleder and Heldt. | | b. | | Knopp. | | Stenhouse. | | Hesse. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C .... | 63·39 | .... | 63·49 | .... | 63·72 | .... | 63·49 | .... | 62·8 | .... | 62·2 |
| H .... | 4·99 | .... | 4·82 | .... | 4·92 | .... | 5·08 | .... | 5·0 | .... | 5·3 |
| O .... | 31·62 | .... | 31·69 | .... | 31·36 | .... | 31·43 | .... | 32·2 | .... | 32·5 |
| | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·0 | .... | 100·0 |

*a* was obtained from *Cladonia rangiferina*, *b* from *Usnea florida* (Rochleder and Heldt). Knop investigated an acid from *Usnea florida ;* Hesse an acid from *Ramalina calicaris.* — According to Hesse's formula, which, indeed, is rendered probable by these considerations, usnic acid bears the same relation to everninic acid as lecanoric to orsellinic acid, whilst evernic acid occupies an intermediate position between the two : —

$$C^{36}H^{18}O^{14} + 2HO = C^{18}H^{10}O^3 + C^{18}H^{10}O^8$$

<p style="text-align:center">Usnic acid.               Everninic acid.</p>

$$C^{34}H^{16}O^{14} + 2HO = C^{18}H^{10}O^8 + C^{16}H^8O^8$$
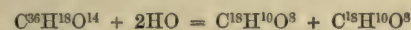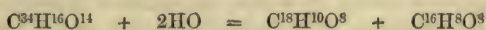
<p style="text-align:center">Evernic acid.          Everninic acid. Orsellinic acid.</p>

$$C^{32}H^{14}O^{14} + 2HO = C^{16}H^8O^3 + C^{16}H^8O^9$$

<p style="text-align:center">Lecanoric acid ¦         Orsellinic acid.</p>

*Decompositions.* 1. Usnic acid subjected to *dry distillation* yields a sublimate of beta-orcin (xiii, 150), together with a distillate of brown resinous liquid, whilst a difficultly combustible charcoal remains behind (Stenhouse). The decomposition is accompanied by the evolution of an inflammable vapour, which has a peculiar odour and violently attacks the respiratory organs (Knop). — 2. According to Knop, it is but little altered by *chlorine ;* according to Stenhouse, it is resinized thereby. Hypochlorite of soda does not colour usnic acid (Hesse). — 3. Decomposed by heating with *oil of vitriol* (Knop). See below. — 4. Dilute *nitric acid* has but little action on usnic acid : the concentrated acid dissolves it to a yellow-brown syrup, from which the usnic acid may be precipitated by water, unchanged at first. The solution slowly evolves red vapours in the cold, and afterwards, on mixing with water, throws down a yellow resin, which, when washed and dried, forms a red-yellow friable mass, exploding when heated, dissolving easily in alcohol, and thereby separable from unchanged usnic acid. Its alcoholic solution is coloured green by agitation with protosulphate of iron (Knop & Schnedermann). — 5. Usnic acid, boiled with an excess of *caustic potash* solution, or with *baryta* or *lime-water*, yields acid resins and beta-orcin; the liquid is coloured red from

some further change in the beta-orcin (Stenhouse). The formation of beta-orcin is represented by the equation

$$C^{36}H^{18}O^{14} + 2HO = 4CO^2 + 2C^{16}H^{10}O^4 \text{ (Hesse)}.$$

A solution of usnic acid in excess of ammonia assumes, when exposed to the air, a wine-red colour from above downwards, the usnic acid being at last converted, by successive steps, into a red colouring matter, which colours the liquid dark wine-red, and remains behind on evaporation. — A solution in excess of alkali reddens more quickly in the air, especially when heated. From a solution which has attained a carmine-red colour, acids precipitate golden-yellow flocks, which dissolve in alcohol with yellow colour, and remain as an amorphous powder on evaporation. The flocks dissolve in caustic potash with carmine-red, and in oil of vitriol with dirty olive-green colour: they melt to a carmine-red mass, and afterwards form a solution of the same colour with oil of vitriol. By the continued action of potash, a black tar is at last produced (Knop). — 6. *Chromic acid* acts violently upon usnic acid (Knop & Schnedermann). — 7. The solution of usnic acid in excess of potash, when heated with *peroxide of lead*, quickly assumes a brown-red colour, and, on addition of an acid, throws down brown flocks, the quantity of which constantly decreases. On continued heating, the liquid becomes lighter-coloured, and at length nearly colourless, the usnic acid being completely oxidized to carbonic acid and water (Schnedermann & Knop).

Usnic acid is not wetted by *water*, and is not soluble therein (Knop). It dissolves in *oil of vitriol* with yellow colour, and is precipitated from the solution by water, unchanged (Knop).

Usnic acid combines with bases, forming *salts*. They are not decomposed by carbonic acid, but other acids precipitate the usnic acid in the form of a nearly white powder, which, when precipitated from an aqueous solution, obstinately retains a portion of the base. The salts of the alkalis are colourless and crystallisable. In the absence of an excess of alkali, they slowly become coloured in the air. The salts of the earthy alkalis, earths, and heavy metals are obtained by precipitation in amorphous flocks, which aggregate in microscopic granules when heated. In presence of an excess of the precipitant, they are generally soluble in hot water, and are thrown down in the amorphous state on cooling. The salts are, for the most part, soluble in alcohol. Ether takes up usnic acid from the salts of the earths and heavy metals (Knop).

*Usnate of Ammonia.* — a. *Neutral.* Usnic acid is suspended in alcohol, into which ammonia gas is passed till solution is effected. The liquid is then allowed to evaporate spontaneously. — The salt crystallises as needles, from which boiling water separates usnic acid containing ammonia (Knop).

b. *Acid.* — Usnic acid absorbs moist ammonia-gas, and forms therewith an acid salt. — When powdered usnic acid is digested in an excess of aqueous carbonate of ammonia, an acid salt is produced which, after the carbonate is poured off, dissolves in water, and is again precipitated by carbonate of ammonia (Knop).

*Usnate of Potash.* — When powdered usnic acid is boiled with

excess of aqueous carbonate of potash, this salt crystallises on cooling, and may be purified by re-crystallisation. — White crystalline laminæ, containing 12·30 p. c. of water (6 at. = 12·32 p. c.) (Hesse), a part of which is given off at ordinary temperatures (Knop). The aqueous solution froths like soap-water, and deposits flocks of an acid salt when much diluted (Knop).

|  | | at 100° and 130°. | | | | Hesse. | Knop. | Stenhouse. mean. |
|---|---|---|---|---|---|---|---|---|
| 36 | C | 216 | .... | | 56·22 | .... | 56·60 | | |
| 17 | H | 17 | .... | | 4·42 | .... | 4·50 | | |
| 13 | O | 104 | .... | | 27·08 | .... | 26·92 | | |
| | KO | 47·2 | .... | | 12·28 | .... | 11·98 | .... 11·04 | .... 11·57 |
| $C^{36}H^{17}KO^{14}$ | .... | 384·2 | .... | | 100·00 | .... | 100·00 | | |

*Usnate of Soda.* — Obtained in the same manner as the potash-salt. Silky, radiated needles, more easily decomposed in the air than the potash-salt. Decomposed by boiling with water, with formation of an acid salt (Knop).

*Usnate of Baryta.* — A slight excess of chloride of barium is added to a hot aqueous solution of the potash-salt, and the whole is heated to boiling, when a snow-white, silky precipitate of the hydrated salt is produced, a small portion only being dissolved. The salt loses its water of crystallisation at ordinary temperatures. By dissolving it in strong alcohol and evaporating the solution, the anhydrous salt is obtained in yellowish-white, crystalline crusts, which do not again dissolve in alcohol (Knop).

|  | | at 100°. | | | | Knop. mean. |
|---|---|---|---|---|---|---|
| $C^{36}H^{17}O^{13}$ | .... ........ | 337 | ........ | . 81·5 | | |
| BaO | ........ | 76·5 | ........ | 18·5 | ........ | 17·41 |
| $C^{36}H^{17}BaO^{14}$ | ........ | 413·5 | ........ | 100·0 | | |

The *lead-salt* is white; the *silver-salt* white, and easily decomposed (Knop). The acid is not coloured by *ferric chloride* (Hesse).

*Usnate of Copper.* — The potash-salt is decomposed by a slightly insufficient quantity of nitrate of copper. — Grass-green, amorphous precipitate, which becomes electric when rubbed (Knop).

|  | | at 100°. | | | | Knop. |
|---|---|---|---|---|---|---|
| 36 | C | 216 | ........ | 57·34 | ........ | 57·15 |
| 17 | H | 17 | ........ | 4·51 | ........ | 4·38 |
| 13 | O | 104 | ........ | 27·74 | ........ | 28·27 |
| | CuO | 39·8 | ........ | 10·41 | ........ | 10·20 |
| $C^{36}H^{17}CuO^{14}$ | ... | 376·8 | ........ | 100·00 | ........ | 100·00 |

Usnic acid is scarcely soluble in cold, and very slightly soluble in boiling *alcohol*. It dissolves difficultly in cold, but more freely in boiling, *ether*, also in boiling *oil of turpentine*, and hot *fatty oils* (Knop).

*Oxyazo-nucleus*  $C^{36}N^2H^{22}O^4$.

# Menispermine.

? $C^{36}N^2H^{24}O^4 = C^{36}N^2H^{22}O^4,H^2$.
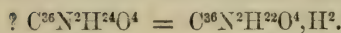
PELLETIER & COUERBE.  *Ann. Chim. Phys.* 54, 196; *Ann. Pharm.* 10, 198.

*Source.*  In the husk of *Cocculus indicus.*

*Preparation.*  The berries, bruised together with the husks, are exhausted with boiling alcohol of 36°; the extract is filtered; the alcohol distilled off; and from the residue (first freed from picrotoxine by treatment with boiling water), the menispermine and paramenispermine are taken up by acidulated water, and thrown down from the solution by ammonia.  The precipitate is dissolved in dilute acetic acid, precipitated by ammonia, and dried; it is then exhausted with alcohol, and the solution is left to evaporate spontaneously, whereby a yellow alkaline resin, crystals of menispermine, and a yellowish mucus are obtained.  The crystals are picked out as far as possible and removed, and the yellow mucus is first freed from resin by means of cold alcohol, and then washed with cold ether, which takes up the remaining menispermine and leaves it behind on evaporation.  The whole of the crystals are purified by rinsing with cold alcohol. — By dissolving the yellow mucus in absolute alcohol and evaporating the solution at 45, paramenispermine is obtained.

*Properties.*  White, semi-transparent, four-sided pointed prisms, resembling cyanide of mercury and melting at 120°.  Tasteless.  Not poisonous.

|   |   |     |   |         |   | Pelletier and Couerbe. |
|---|---|-----|---|---------|---|---------|
|   |   |     |   |         |   | *mean.* |
| 36  C | 216 | ........ | 72·00 | ........ | 70·45 |
| 2  N | 28 | ........ | 9·35 | ........ | 9·45 |
| 24  H | 24 | ........ | 8·00 | ........ | 8·01 |
| 4  O | 32 | ........ | 10·65 | ........ | 12·09 |
| $C^{36}N^2H^{24}O^4$ | 300 | ........ | 100·00 | ........ | 100·00 |

The formula was proposed by Pelletier and Couerbe.  According to Liebig (*Ann. Pharm.* 10, 208) it is to be regarded as very doubtful.

*Decompositions.*  1. Menispermine is decomposed by *heating* in a glass tube, and leaves charcoal. — 2. Concentrated *nitric acid* converts it into resin and oxalic acid.

Menispermine is insoluble in *water.*

It dissolves in dilute *acids* and forms therewith salts, from the solutions of which alkalis precipitate menispermine.

*Sulphate of Menispermine.* — Oil of vitriol dissolves menispermine when warmed, and deposits it again on addition of aqueous ammonia. — With dilute sulphuric acid, needles or prisms are obtained, which melt to a wax at 105°, redden and evolve hydro-sulphuric acid when

more strongly heated. The salt has an alkaline reaction. Contains 15 p. c. of water, 6·87 of sulphuric acid, and 78·13 of menispermine, or, according to Pelletier & Couerbe, 2 atoms of menispermine and 10 atoms of water to 1 atom of sulphuric acid.

Menispermine dissolves in cold, and more freely in warm *alcohol* and *ether*.


## Paramenispermine.

PELLETIER & COUERBE. *Ann Chim. Phys.* 54, 126; *Ann Pharm.* 10, 200.

*Source.* In the husks of *Cocculus indicus.*

*Preparation.* See page 52.

*Properties.* Four-sided prisms with rhombic base, or radiated star-shaped masses. Melts at 250° and sublimes undecomposed. Has the same composition as menispermine.

Paramenispermine is insoluble in water. It dissolves in dilute *acids*, but does not form salts, and is decomposed by boiling acids.

Soluble in absolute *alcohol*, nearly insoluble in *ether*.


*Primary Nucleus* $C^{36}H^{34}$.


## Hydrocarotin.

$$C^{36}H^{20}O^2 \;=\; C^{26}H^{30}, O^2.$$
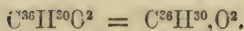
AUG. HUSEMANN. *Dissert. über Carotin und Hydrocarotin.* Gött. 1860.

First observed by Bödeker; investigated by Husemann. — Occurs, together with carotin, in the roots of the cultivated *Daucus Carota.*

The alcoholic solution of hydrocarotin and mannite, obtained in the preparation of carotin (p. 14), deposits, on cooling, a red-brown slimy sediment, which being removed and the liquid set aside for a week, a mixture of mannite and hydrocarotin crystallises out. The mother-liquor, when concentrated, yields more hydrocarotin, but of a darker colour, till at last a thick syrup remains. The mannite is removed by solution in water, and the hydrocarotin is purified by repeated re-crystallisation from the smallest possible quantity of boiling alcohol, and at last by boiling with water.

*Properties.* Large, colourless, very thin, soft, flexible laminæ, possessing a strong silky lustre. Crystallises from ether in flat rhombic tables. Inodorous, tasteless. Floats on water like a fatty body, without being wetted. — At 100° it is hard and brittle; a little above 100° yellowish and soft; a few degrees below its melting-point, dark-yellow. Melts at 126·5° without losing weight, and solidifies, on cooling, to a brittle resin, which cannot be re-crystallised.

|        |        |     |        |        |        | Husemann. |
|        |        |     |        |        |        | *mean.*   |
| 36 C  | ........ | 216 | ........ | 82·44 | ........ | 82·32     |
| 30 H  | .. ... | 30  | ........ | 11·41 | ........ | 11·53     |
| 2 O   | ........ | 16  | ........ | 6·15  | ........ | 6·15      |
| C³⁶H³⁰O² .... | | 262 | ........ | 100·00 | .... ... | 100·00 |

*Decompositions.* 1. When *heated* above its melting-point, it turns red, and at 280° carbonises, giving off white empyreumatic vapours and a colourless oil. — 2. With *iodine, bromine,* and *chlorine* it forms substitution-products containing 1 at. iodine, 3 at. bromine, and 4 at. chlorine. — 3. It is not altered by concentrated nitric acid; fuming *nitric* or *nitro-sulphuric acid* dissolves it, forming a colourless solution, from which water precipitates a white amorphous nitro-compound, easily soluble in ether, alcohol, and benzene, and difficultly soluble in bisulphide of carbon. — 4. *Oil of vitriol* colours hydrocarotin ruby-red, dissolves it, on warming, with bright-red colour, and carbonises it on boiling. From the solution prepared by gently warming, water throws down the whole of the hydrocarotin in the amorphous state, nothing remaining in solution. — 5. Hydrocarotin is not altered by boiling solution of caustic potash; when melted with *hydrate of potash* it is converted into a yellow amorphous mass, which reddens at 80°, and melts at 120° to a dark-red viscid liquid.

Hydrocarotin is not altered by dilute or concentrated acids, even on addition of oxide of manganese, chromate of potash, or peroxide of lead; nor by ferricyanide of potassium, permanganate of potash, sulphurous acid, hydrochloric acid gas, hydrosulphuric acid, or hydrosulphate of ammonia.

*Combinations.* *With Water.* — A solution of hydrocarotin in bisulphide of carbon containing water yields, at a low temperature, crystals which lose their water at ordinary temperatures.

Alcoholic hydrocarotin does not precipitate either *metallic salts* or *tannic acid.*

Hydrocarotin dissolves in boiling *alcohol,* crystallising therefrom almost entirely on cooling. It dissolves easily in *bisulphide of carbon, ether, choloroform, benzene,* and *volatile oils;* also in *fixed oils,* even in the cold.

<div align="center">

*Iodine-nucleus* C³⁶IH²⁹.

### Iodo-hydrocarotin.

C³⁶IH²⁹O² = C³⁶IH²⁹,O².

</div>
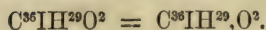
HUSEMANN. *Dissertation über Carotin und Hydrocarotin.* Gött. 1860.

Hydrocarotin, exposed to sunshine with vapour of iodine, assumes a darker colour, becoming black at last, and increases about 49·6 p. c. in weight (calc. 48·09 p. c.). The product is thrown down from its ethereal solution by weak alcohol in the form of a yellow-

white powder, which turns soft and dark-red at 70° to 80°. It dissolves with difficulty in *alcohol*, easily in *ether, bisulphide of carbon*, and *benzene*.

*Bromine-nucleus* $C^{36}Br^3H^{27}$.

## Terbromo-hydrocarotin.

$$C^{36}Br^3H^{27}O^2 = C^{36}Br^3H^{27}, O^2.$$

HUSEMANN. *Dissert. über Carotin und Hydrocarotin.* Gött. 1860.

Hydrocarotin becomes brown and soft in vapour of bromine, giving off hydrobromic acid, and in 24 hours is converted into a brittle, red-brown mass, which is precipitated from its ethereal solution by alcohol, as a pale-yellow powder.

Contains 47·7 to 48·7 p. c. of bromine ($C^{36}Br^3H^{27}O^2 = 48·09$ p. c. Br). — It assumes a darker colour and softens at 162°, blackens at 170°, and carbonises without melting. — The solution in ether or benzene is coloured red by boiling with alcoholic potash, and leaves, on evaporation, a yellow-red body, free from bromine, soluble in bisulphide of carbon with red colour: probably carotin.

Terbromo-hydrocarotin is insoluble in boiling *alcohol*, and difficultly soluble in boiling *ether*. It dissolves easily in *bisulphide of carbon* and *benzene*, and does not crystallise from the solution.

*Chlorine-nucleus* $C^{36}Cl^4H^{26}$.

## Quadrichlor-hydrocarotin.

$$C^{36}Cl^4H^{26}O^2 = C^{36}Cl^4H^{26}, O^2.$$
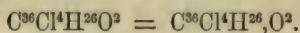
HUSEMANN. *Dissert. über Carotin und Hydrocarotin.* Gött. 1860.

Chlorine gas is passed over pulverulent hydrocarotin for three days, and the hydrochloric acid formed is expelled at 100° by dry air, the hydrocarotin then increasing about 55·36 p. c. in weight (calc. 52·67 p. c.). The product is repeatedly boiled with alcohol, and afterwards dissolved in ether-alcohol and precipitated by water. — Or, hydrocarotin suspended in water is subjected to the prolonged action of chlorine gas.

White powder, containing on an average, 35·17 p. c. of chlorine (calc. for $C^{36}Cl^4H^{26}O^2 = 35·5$ p. c. Cl.). Obtained from its solutions as a brown-yellow, amorphous, brittle resin. It softens, and turns dark-red at 80°, melts at 118°, and remains red on cooling.—Alcoholic potash converts it into a body free from chlorine.

Soluble in *ether* and *absolute alcohol* ; easily soluble in *benzene* and *bisulphide of carbon*.

*Primary Nucleus* $C^{36}H^{33}$; *Oxygen-nucleus* $C^{36}H^{26}O^{6}$.

## Glycyrretin.

$? \; C^{36}H^{26}O^{8} \; = \; C^{36}H^{26}O^{6},O^{2}.$
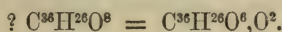
GORUP-BESANEZ. *Ann. Pharm.* 118, 241.

On boiling a solution of 1 part of glycyrrhizin in 20 parts of water, together with the precipitate at first produced, with 1 part of concentrated hydrochloric acid for four hours, renewing the water as it evaporates, the precipitate melts to a brown-red mass, which at last becomes brittle, the liquid remaining of a wine-yellow colour, and containing sugar in solution. The brown-red mass is glycyrretin ; it may be decolorised by treating its alcoholic solution with animal charcoal, and is then a yellowish-white, friable substance.

It contains, in various preparations, from 73 to 75 p. c. of carbon, and 9·53 to 10·39 of hydrogen, not agreeing with the formula $C^{36}H^{26}O^{8}$ (calc. 70·5 C. 8·5 H.), which is therefore probable only from the formula of glycyrrhizin, $C^{48}H^{36}O^{18}$, and on the supposition that the decomposition takes place according to the equation :

$$C^{48}H^{36}O^{18} + 2HO = C^{36}H^{26}O^{8} + C^{12}H^{12}O^{12}.$$
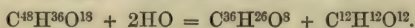
Probably the product first formed itself undergoes change.

Brown-yellow glycyrretin has a very bitter taste. It does not melt in boiling water, but melts easily when heated on platinum-foil, taking fire, and burning with a very smoky flame, like a resin. It dissolves in oil of vitriol, forming an amaranth-red solution, which changes, on standing, to violet, and on dilution with water to purple-violet, with deposition of a blue-black precipitate. It is precipitated by acids from its brown-red solution in ammonia or aqueous alkalis. — Dissolves in alcohol, from which it is precipitated by water, and rather less easily in ether.

*Glucoside of Glycyrretin.*

## Glycyrrhizin.

PFAFF. *System. der Mat. med.* 1, 187.
ROBIQUET. *Ann. Chim.* 72, 143.
DÖBEREINER. *Elemente der pharm. Chemie*, 194.
BERZELIUS. *Pogg*, 10, 243 ; *Lehrb.* 3, 356.
TROMMSDORFF. *Taschenbuch*, 1827, 1.
L. A. BACKER. *Repert.* 88, 176.
A. VOGEL. *J. pr. Chem.* 28, 1 ; abstr. *Ann. Pharm.* 48, 347.
LADE. *Ann. Pharm.* 59, 224 ; *J. pr. Chem.* 40, 121.
GORUP-BESANEZ. *Ann. Pharm.* 118, 236 ; abstr. *J. pr. Chem.* 84, 246 ; *Chem. Centr.* 1861, 798 ; *Rép. Chim. pure*, 4, 30 ; *Kopp's Jahresb.* 1861, 757.

*Glycion.* Pfaff's *Sweet Extractive.* Berzelius's *Liquorice sugar.*

*Source.* In the roots of *Glycyrrhiza glabra* and *Gl. echinata.* — In Monesia bark (Derosne, Henry & Payne, *J. Pharm.* 27, 25.)

Berzelius extracted from the leaves of *Abrus præcatorius*, a bitter-sweet substance allied to glycyrrhizin, obtained in the same way, and exhibiting the same reactions with acids, alkalis, and metallic salts. — The root of *Polypodium vulgare* contains a similar, but more easily decomposed substance. Its aqueous infusion tastes like that of liquorice ; it is precipitated by sulphuric acid after some hours, the liquid losing, at the same time, its sweet taste. The precipitate assumes a yellow colour, and when dissolved in alcohol and treated with carbonate of potash, yields a red, but not sweet substance, easily soluble in water ; neither does the precipitate thrown down from the infusion by neutral acetate of lead, yield any sweet substance when decomposed by hydrosulphuric acid (Berzelius).

*Sarcocolla*, the substance which exudes from *Penaen Sarcocolla* and *P. mucronata*, contains a sweet substance allied to glycyrrhizin (Döbe-reiner), or to the sweet substance of *Polypodium* (Desfosses, *J. Pharm.* 14, 276). According to Pelletier (*Bull. Pharm.* 5, 5 ; *Ann. Chim. Phys.* 51, 198 ; *Berz. Jahresbr.* 13, 314), it is resolved, by treatment with ether, into a resin which dissolves, and a residue of gum and *sarcocollin*, the latter of which dissolves in alcohol. Sarcocollin contains 56·48 p. c. C., 8·34 H., and 35·18 O. It is soluble in water and alcohol, but insoluble in ether, has a bitter-sweet taste, and is converted into oxalic acid by nitric acid (Pelletier). See also Thomson (*System der Chemie, Wolff's trans.*, 4, 37) ; Pfaff (*System der Mat. med.* 1, 190) ; Johnston (*J. pr. Chem.* 23, 397 ; *Ann. Pharm.* 37, 35).

*Preparation of glycyrrhizin.* From the Russian, not from the Spanish liquorice root, the latter yielding a coloured glycyrrhizin, difficult to purify (Gorup-Besanez). 1. An aqueous extract of the roots is boiled down rapidly, and the green-brown coagulum which forms is removed ; the filtrate is then concentrated and precipitated by dilute sulphuric acid (the deposited nitrogenous substance being first separated if necessary). The pale-yellow flocks first thrown down are converted after some hours into a dark-brown tough mass, which is washed with water by decantation, till the washings are no longer rendered cloudy by salts of baryta. The residue is dissolved in alcohol of 82 p. c. ; to the solution (not too concentrated), a small quantity of ether is added ; and the brown resin which is deposited after some time is removed. The ether-alcoholic solution is evaporated over the water-bath, and the residue is purified by again dissolving it in alcohol, mixing the solution with ether, whereby a little more resin is precipitated ; filtering, and evapo-rating to dryness (Gorup-Besanez). A similar process was previously adopted by Lade, who, however, did not purify his product with ether. Robiquet uses vinegar to precipitate the aqueous extract. Berzelius precipitates with sulphuric acid ; dissolves the washed precipitate, which still contains sulphuric acid, in alcohol ; precipitates the acid by careful addition of carbonate of potash, and evaporates the filtrate. Martin (*Pharm. Viertelj.* 10, 259 ; *Kopp's Jahresb.* 1860, 551), precipi-tates the extract prepared with cold water, with bitartrate of potash ; digests the dried precipitate with alcohol at a gentle heat ; filters the solution to remove bitartrate of potash and other insoluble salts ; and evaporates to dryness.

2. The roots are exhausted with boiling water, and to the filtered

liquid basic acetate of lead is cautiously added; the precipitate is washed and decomposed under water by hydrosulphuric acid, and the filtrate is boiled and evaporated. The residue is purified by repeated solution in alcohol and evaporation (Vogel). The product thus obtained probably still requires to be purified according to 1.

To prepare glycyrrhizin from the *Succus Liquiritii* of commerce, C. Rump (*N. Repert.* 4, 153) exhausts it with weak ammonia-water, precipitates the glycyrrhizin with hydrochloric or acetic acid; dissolves the precipitate in ammonia-water; removes magnesia and lime by the addition of phosphate and oxalate of ammonia; and throws down the glycyrrhizin by acetic acid. The gelatinous precipitate is dried and triturated, and afterwards washed with water.

*Properties.* Amorphous, yellowish-white powder, having an intense bitter-sweet taste (Gorup-Besanez). According to Vogel, brown-yellow; according to others, a brown, transparent, brittle, shining mass. — Its alcoholic solution smells like infusion of liquorice-root; the aqueous solution reddens litmus strongly (Lade). It is without action on polarised light (Ventzke, *J. pr. Chem.* 25, 65).

| | | | | Vogel. mean. | | Lade. mean, *at* 100° | | Gorup-Besanez. mean. |
|---|---|---|---|---|---|---|---|---|
| 48 C | 288 | .... | 61·54 | .... | 61·65 | .... | 61·02 | .... | 61·46 |
| 36 H | 36 | .... | 7·69 | .... | 7·64 | .... | 7·25 | .... | 7·71 |
| 18 O | 144 | .... | 30·77 | .... | 30·71 | .... | 31·73 | .... | 30·83 |
| C⁴⁸H³⁶O¹⁸ | 468 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 |

Lade's glycyrrhyzin contained a little nitrogen. Vogel proposed the formula C¹⁶H¹²O⁶, Lade the formula C³⁶H²⁴O¹⁴: Gorup-Besanez, who recognised glycyrrhizin as a glucoside, considered the above a probable formula.

*Decompositions.* 1. Glycyrrhizin *heated* to 200° melts to a dark-brown, transparent mass (Lade), takes fire, and burns with a luminous, smoky flame, frothing up and evolving resinous vapours, which redden litmus, and have an odour of burnt sugar (Trommsdorff). When blown into the flame of a candle, it burns like lycopodium (Berzelius). 2. It reduces sesquioxide of chromium from a mixture of *bichromate of potash* and sulphuric acid, and is violently decomposed by *peroxide of lead* (Gorup-Besanez). — 3. Decomposed by cold, and more rapidly by hot *nitric acid*, a large quantity of nitric oxide gas being liberated, and a bright-yellow body deposited, whilst oxalic acid and pale-yellow crystals of a nitro-compound [probably styphnic acid (xi, 228)] are likewise formed (Gorup-Besanez. Lade).

By boiling with nitric acid, Robiquet obtained a yellow, tough mass, which was resolved by water into an artificial bitter, and a white, tasteless residue.

On boiling a concentrated infusion of liquorice with nitric acid till all frothing has ceased, precipitating the product with water, boiling the washed precipitate with concentrated nitric acid, and pouring the solution into water, with constant stirring, there is thrown down a light, yellow, very bitter powder, which reddens litmus, burns on platinum-foil like wax, is slightly soluble in water, insoluble in boiling concentrated nitric acid, but easily soluble in alcohol and in aqueous alkalis, forming with the last, orange-coloured solutions from which it is precipitated by acids. This substance has the composition *a* (Lade).

Glycyrrhizin, subjected to the same treatment, yields a body having the composition $b$. When glycyrrhizin is added to cold nitro-sulphuric acid, a yellowish-white, amorphous powder ($c$) is deposited. This body resembles that obtained by Lade, and is, like it, free from nitrogen (Gorup-Besanez).

|  |  |  |  |  | Lade.<br>$a$. |  | Gorup-<br>Besanez.<br>$c$. |
|---|---|---|---|---|---|---|---|
| 48 | C | 288 | ........ | 57·83 | 57·23 | ........ | 57·04 |
| 34 | H | 34 | ........ | 6·82 | 6·03 | ........ | 6·66 |
| 22 | O | 176 | ........ | 35·35 | 36·74 | ........ | 36·30 |
| $C^{48}H^{34}O^{22}$ | | 498 | ........ | 100·00 | 100·00 | ........ | 100·00 |

|  |  |  |  |  | Gorup-<br>Besanez.<br>$b$. |
|---|---|---|---|---|---|
| 48 | C | 288 | ........ | 61·80 | 60·95 |
| 34 | H | 34 | ........ | 7·29 | 7·27 |
| 18 | O | 144 | ........ | 30·91 | 31·78 |
| $C^{48}H^{34}O^{18}$ | | 466 | ........ | 100·00 | 100·00 |

4. Glycyrrhizin dissolves in *oil of vitriol*, forming a red-brown solution (brown according to Lade), from which water precipitates grey-brown flocks. It is decomposed by boiling with *dilute acids*, glycyrretin being deposited and sugar remaining in solution (Gorup-Besanez). The decomposition may perhaps be expressed thus:

$$C^{48}H^{36}O^{18} + 2HO = C^{36}H^{26}O^{8} + C^{12}H^{12}O^{12},$$
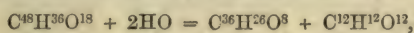
the equation requiring 65·3 p. c. of glycyrretin and 38·4 p. c. of sugar, whilst 65·4 p. c. of glycyrretin and 17·5 p. c. of sugar are obtained (Gorup-Besanez). — When the decomposition is effected with hydrochloric acid, and the solution is filtered from glycyrretin, the acid being afterwards removed by acetate of silver, and the excess of silver by hydrosulphuric acid, the sugar is left on evaporation in the form of a brownish, very sweet syrup, which does not crystallize. It behaves like grape-sugar with alkaline solutions of copper and with potash, oxide of bismuth, gallic and sulphuric acids, and yeast (Gorup-Besanez).

Glycyrrhizin does not reduce *potassio-cupric tartrate* at temperatures of 75° to 100° (Mathey, *N. Br. Arch.* 72, 293). It is not susceptible of fermentation (Lade), and is not decomposed by *emulsin* (Gorup-Besanez).

*Combinations*. Glycyrrhizin dissolves with difficulty in cold, and more easily in hot *water*, forming a yellow solution, from which a small portion is deposited in resinous drops on cooling (Gorup-Besanez). A hot saturated solution solidifies to a brown jelly on cooling (Lade).

*Mineral* and *vegetable acids* produce, in aqueous solutions of glycyrrhizin, curdy precipitates, which in very dilute solutions appear only after some time. They dissolve slightly in pure, but not in acidulated water (Berzelius, Döbereiner). According to Berzelius and Vogel, these precipitates are to be regarded as combinations of gly-

cyrrhizin with acids. That produced by *sulphuric acid* contains, after washing, 7·34 p. c. of sulphuric acid and 92·66 p. c. of glycyrrhizin (Vogel). Backer and Lade, on the contrary, found it perfectly free from sulphuric acid. — The precipitate thrown down by acetic acid (Berzelius's acetate of glycyrrhizin) dissolves more freely in boiling water than the sulphuric precipitate, and forms, when dry, nearly white, sweet scales containing acetic acid (Berzelius). — Acetic acid precipitates the infusion of liquorice-root, but not aqueous glycyrrhizin. It dissolves the precipitates produced by other acids (Backer).

Glycyrrhizin combines with bases (Berzelius). *Ammonia* and *alkalis* render it more soluble in water (Lade, Rump). They dissolve it with deep red-yellow colour, evolving a peculiar odour (Gorup-Besanez). Glycyrrhizin expels carbonic acid from the carbonates of potash, baryta, and lime. After filtering and evaporating, there remains an extract, which has a sweet taste, provided the alkali does not predominate. The extract is easily soluble in water, less freely in alcohol (Berzelius).

*Chloride of barium* throws down from aqueous glycyrrhizin a compound soluble in hydrochloric acid (Vogel). *Sulphate of magnesia* (Gorup-Besanez), *sesquichloride of iron*, *protochloride of tin*, and *sulphate of copper* also produce precipitates. *Ferrous* and *mercurous salts*, and *corrosive sublimate*, on the contrary, do not (Berzelius, Gorup-Besanez). *Nitrate of silver* produces a cloudiness in aqueous glycyrrhizin (Gorup-Besanez). It throws down a white, easily soluble precipitate (Lade). The precipitates produced by ferric sulphate and sulphate of copper in infusion of liquorice are soluble in excess of caustic potash (Lassaigne, *J. Chim. méd.* 18, 418). The precipitates formed with salts of the metals give up a little glycyrretin to warm alcohol (Döbereiner, Berzelius). When they are decomposed under water by hydrosulphuric acid, the water takes up little or nothing, the glycyrrhizin remaining in combination with the acid (Berzelius).

*Lime-compound.* — Aqueous glycyrrhizin does not precipitate chloride of calcium (Gorup-Besanez). When an infusion of liquorice prepared with cold water, is boiled with milk of lime, and the product is collected and washed, there remains on the filter a dirty yellow residue, which is difficultly soluble in water, and imparts thereto a sweet taste. This body is resolved by treatment with carbonic acid under water into carbonate of lime and the lime-compound of glycyrrhizin, the latter of which is soluble in water, but insoluble in alcohol (Lade). Aqueous glycyrrhizin-lime deposits crystals of carbonate of lime when exposed to the air (Kuhlmann, *Ann. Pharm.* 27, 22).

*Two-thirds.* — Alcoholic glycyrrhizin is precipitated by alcoholic chloride of calcium, and the pale-yellow precipitate is washed with alcohol (Gorup-Besanez).

|  |  |  |  |  |  | Gorup-Besanez. |
|---|---|---|---|---|---|---|
| 96 C | | 576 | ....... | 54·54 | ....... | 53·86 |
| 76 H | | 76 | ....... | 7·19 | ....... | 7·08 |
| 40 O | | 320 | ....... | 30·30 | ....... | 30·77 |
| 3 CuO | | 84 | ....... | 7·97 | ....... | 8·29 |
| 2C⁴⁸H³⁶O¹⁸,3CuO,4HO | .... | 1056 | ....... | 100·00 | ....... | 100·00 |

*Lead-compound.* An aqueous solution of glycyrrhizin is rendered turbid (precipitated according to Berzelius and Vogel) by neutral acetate of

lead, and is precipitated by the basic acetate and by an ammoniacal
solution of the neutral acetate (Gorup-Besanez). On precipitating
alcoholic glycyrrhizin with aqueous neutral acetate of lead, filtering
when the further addition of a small quantity of the acetate no
longer causes a precipitate, and then adding a large quantity of the
aqueous acetate, dark-yellow granules and resinous drops are pre-
cipitated, the latter of which are soluble in alcohol. Basic acetate of
lead, added to the filtrate, throws down a further portion, but not the
whole, of the glycyrrhizin (Gorup-Besanez).

a. *With 6 at. of Lead-oxide.* — An aqueous solution of neutral acetate
of lead containing a little ammonia, is added to aqueous glycyrrhizin,
while constantly stirring, till the greater part of the glycyrrhizin is
precipitated. The yellowish-white flocks are washed, and dried at
100°. — Pale-yellow powder, insoluble in water and alcohol (Gorup-
Besanez).

|  |  | *at* 100°. |  |  | Gorup-Besanez. |
|---|---|---|---|---|---|
| 48 C | ............................... | 288 | ........ | 24·52 | ........ | 24·07 |
| 40 H | ............................... | 40 | ........ | 3·46 | ........ | 2·92 |
| 22 O | ............................... | 176 | ........ | 14·94 | ........ | 16·13 |
| 6 PbO | ............................... | 670·2 | ........ | 57·08 | ........ | 56·88 |
| $C^{48}H^{36}O^{18},6PbO,4HO$ | .... | 1174·2 | ........ | 100·00 | ........ | 100·00 |

b. *With 3 atoms of Lead-oxide?* — Glycyrrhizin dissolved in weak
alcohol is precipitated by cold aqueous neutral acetate of lead, and
the precipitate is washed with alcohol. — Yellow, amorphous powder
(Lade). Contains 41·59 p. c. of oxide of lead (Vogel).

|  |  | *at* 100°. |  |  | Lade. |
|---|---|---|---|---|---|
| 48 C | ......................... | 288 | ........ | 35·86 | ........ | 37·46 |
| 36 H | ......................... | 36 | ........ | 4·48 | ........ | 4·37 |
| 18 O | ......................... | 144 | ........ | 17·92 | ........ | 18·37 |
| 3 PbO | ......................... | 335·1 | ........ | 41·74 | ........ | 39·80 |
| $C^{48}H^{36}O^{18},3PbO$ | .... | 803·1 | ........ | 100·00 | ........ | 100·00 |

c. The precipitate b, after washing with water and drying, con-
tains 45·98 p. c. C., 5·49 H., 23·89 O., and 24·64 PbO, or about 4 at. of
oxide of lead to 3 at. of glycyrrhizin.

Glycyrrhizin dissolves quickly and abundantly in *alcohol*, especially
in absolute alcohol (Vogel, Lade). It dissolves completely in warm
*ether* (Gorup-Besanez). Lade found it insoluble in ether. It is not
precipitated by *infusion of galls* (Berzelius). It is withdrawn from its
aqueous solution by *animal charcoal* containing lime (Lade).

*Appendix to Glycyrrhizin.*

## Ononis-glycyrrhizin.

REINSCH. *Repert.* 76, 27.
HLASIWETZ. *Wien. Acad. Ber.* 15, 165.

*Ononid (Reinsch).* — Occurs in the dried roots of *Ononis spinosa,* and
is perhaps produced from true glycyrrhizin contained therein, during
drying (Hlasiwetz).

*Preparation.* 1. An aqueous decoction of the roots is precipitated with dilute sulphuric acid; and the brown flocks are washed with cold water, dried, and repeatedly treated with absolute alcohol, until the residue left on evaporation is perfectly soluble in absolute alcohol. — 2. When an alcoholic extract of the roots is evaporated to a syrup (the onocerin being first crystallised out) and allowed to stand for some days, a deposit of resin is thrown down, after which the clear liquid is to be separated and precipitated with water and dilute sulphuric acid. The precipitate is purified as in 1. — 3. If the brown resin obtained as in 2 is dissolved in alcohol and precipitated by alcoholic neutral acetate of lead, and the brown precipitate is decomposed by hydrosulphuric acid under water, the solution filtered from sulphide of lead, leaves, when evaporated, a brown, shining extract, triturable to a light-brown powder which behaves like glycyrrhizin (Hlasiwetz). Reinsch proceeds in the same way as Berzelius in the preparation of glycyrrhizin (p. 57).

Dark-yellow, amorphous, brittle mass, tasting at first bitter and afterwards persistently sweet (Reinsch, Hlasiwetz). Cakes together in the mouth to a resin. Has an acid reaction (Hlasiwetz).

|  | Calculation according to Hlasiwetz. |  |  |  |  | Hlasiwetz. |  |  |  |  |
|  |  |  |  |  |  | *a.* |  | *b.* |  | *c.* | | *d.* |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 36 C | 216 | .... | 59·01 | .... | 59·1 | .... | 59·6 | .... | 57·8 | .... | 61·5 |
| 22 H | 22 | .... | 6·01 | .... | 6·2 | .... | 6·0 | .... | 6·4 | .... | 6·3 |
| 16 O | 128 | .... | 34·98 | .... | 34·7 | .... | 34·4 | .... | 35·8 | .... | 32·2 |
| C³⁶H²²O¹⁶ .... | 366 | .... | 100·00 | .... | 100·0 | .... | 100·0 | .... | 100·0 | .... | 100·0 |

*a* and *b* were prepared according to 1, *c* according to 2, and *d* according to 3. Hlasiwetz gives for *c* the formula C³⁶H²³O¹⁷, and for *d* the formula C³⁶H²²O¹⁴.

Ononis-glycyrrhizin melts when heated, with strong intumescence, gives off acid vapours, and burns with a smoky flame, leaving charcoal (Reinsch).

The aqueous solution gives an abundant white precipitate with *sulphuric acid*. Precipitates are also produced by *neutral acetate of lead*, *acetate of copper*, *mercurous nitrate*, and *nitrate of silver*, but not by *tartar-emetic* or *tincture of galls* (Reinsch).

Dissolves freely in *alcohol*.

*Primary Nucleus* C³⁶H³⁴.

## Oleic Acid.

$$C^{36}H^{34}O^4 = C^{36}H^{34},O^4.$$
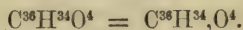
CHEVREUL. *Ann. Chim.* 94, 90, and 263. — *Ann. Chim. Phys.* 2, 358. — *Recherches sur les corps gras*, 75.

BRACONNOT. *Ann. Chim.* 93, 250.

LAURENT. *Ann. Chim. Phys.* 65, 149; *Ann. Pharm.* 28, 253. — *Ann. Chim. Phys.* 66, 154.

VARRENTRAPP. *Ann. Pharm.* 35, 196.

C. BROMEIS. *Ann. Pharm.* 57, 38.

HEINTZ. *Pogg.* 83, 555; 89, 583; 90, 143.

BERTHELOT. *N. Ann. Chim. Phys.* 41, 243.

Chevreul's *Graisse fluide. Acide oléique.* Braconnot's *Huile. — Elaïnsäure.* Discovered by Chevreul in 1811, and first prepared pure by Gottlieb, who also established its formula. Gottlieb and Heintz showed that the oleic acid of butter, which Bromeis supposed to be a peculiar body, is identical with common oleic acid.

Concerning the moringic acid of Walter and the filixolic acid of Luck, see *Appendix to Oleic acid.*

*Source.* Occurs as triolein in most (non-drying) liquid and solid fats. (See below.)

In the bile of men, oxen, pigs, and bears (Chevreul). In the *Mineralmoor* of Marienbad (Lehmann). — It does not occur in castor-oil or spermaceti (or only in very small quantity) (Heintz), nor in wax (Thénard, Redtenbacher), the last substance yielding no sebacic acid when subjected to dry distillation. — Concerning the occurrence of oleomargarin, see under olive-oil; concerning oleophosphoric acid (xvi., 483).

*Preparation.* Almond-oil (olive-oil, goose-fat, butter, or other fat containing olein) is saponified by boiling with caustic potash, and the soap is decomposed by dilute hydrochloric acid. The separated fatty acids are then maintained at a temperature of 100° for several hours with oxide of lead, and the mixture of lead-salts thus obtained is treated with cold ether, which takes up the oleate, but leaves the salts of the solid fatty acids undissolved. The ethereal solution, when shaken with excess of dilute hydrochloric acid, throws down chloride of lead, which sinks to the bottom of the watery layer, whilst oleic acid remains dissolved in the ether. Lastly, the ether is distilled off, and the acid freed from adhering water by evaporation (Varrentrapp, Bromlis).

*Purification.* Oleic acid, prepared as above, still contains oxidized products and colouring matters, to remove which, its solution in a large excess of ammonia is precipitated by chloride of barium; the precipitate is dried and boiled repeatedly with fresh portions of alcohol; and the salt which is deposited on cooling is re-crystallised once or twice from alcohol. It is then decomposed by tartaric acid, and the separated oleic acid is washed with water to remove adhering tartaric acid (Gottlieb).

Or, the acid obtained from the lead-salt is cooled down, in small portions, to 6° or 7°, when it solidifies to a crystalline mass, which is pressed between folds of blotting-paper. The solid and purer acid is thus separated from the fluid portion, which contains oxidised products. By repeatedly melting, cooling, and pressing the crystallised portion, at last with addition of a little alcohol, the impurities are completely removed (Bromeis).

Inasmuch as oleic acid readily absorbs oxygen, all the operations should be conducted with the least possible exposure to the air, more especially when the acid is subjected to a temperature of more than 10° (Bromeis). — In digesting the acid separated from the potash-soap with oxide of lead, the quantity of oxide used should be such as to saturate only a portion of the oleic acid, as in that case the solid fatty acids are completely separated, and less ether is afterwards required to exhaust the lead-salt (Varrentrapp). — The baryta-salt is to be crystallised from moderately-hot strong alcohol; in boiling alcohol it melts to a tough, dark mass (Saalmüller). Tartaric acid is preferable

to hydrochloric acid for decomposing the oleates of the alkalis, since the latter is apt to colour oleic acid. Moreover, by using tartaric acid it is easier to remove the whole of the alkali (Varrentrapp).

From the mixture of stearate (margarate) and oleate of potash obtained by saponification, Chevreul separates the first two acids as bi-acid salts, in the manner described at page 355, vol. xvi., and afterwards decomposes the mother-liquor with tartaric acid, the oleic acid then rising to the surface in the form of an oil. It is washed with hot water, cooled, filtered from the margaric acid which crystallises out, and freed from acetic acid and colouring matter, either by solution in 12 parts of alcohol and precipitation with water, or by converting it into a baryta-salt. The latter, Chevreul boils with water, which takes up acetic acid and colouring matter, and re-crystallises from alcohol. —If the potash-soap obtained by saponifying human fat be digested, in as dry a state as possible, in alcohol of sp. gr. 0·821, the alcohol is found, after 24 hours, to have taken up principally oleate of potash, which may be freed from margaric acid dissolved at the same time by evaporating the solution, treating the residue with cold absolute alcohol, evaporating the filtrate, &c. It is afterwards to be purified as above (Chevreul).

The coloured oleic acid of stearin works is freed from the greater part of the solid fatty acids by filtration at 0°. After separation from its lead-salt, it is to be again saponified with an alkali and salted out with chloride of sodium, with addition of carbonate of soda. In this way only, and not by treatment with animal charcoal, can the colouring matters be removed (Varrentrapp). Berthelot filters commercial oleic acid twice at 0°; neutralises with caustic potash; dissolves in two parts of alcohol; filters the cold solution; precipitates with chloride of barium; and purifies the baryta-salt as above. — When *cantharides' fat* is employed, the lime-soap may also be treated with ether instead of the lead-soap; or the fatty acids of cantharides' fat are dissolved in 5 or 6 parts of alcohol of 85 p. c.; the solution is precipitated with alcoholic neutral acetate of lead; and the precipitate is dissolved in warm acetic acid and allowed to stand for 24 hours, whereupon, palmitate and stearate of lead crystallise out, whilst the oleate of lead remains in solution and is thrown down from the filtrate by ammonia (Gössmann).

The oleate of baryta obtained from *butter* (and from beef and mutton suet) by Gottlieb's method, contains a salt richer in baryta, the presence of which renders the following process necessary. The salt is exhausted with cold ether, and re-crystallised from a large quantity of hot alcohol; it is then allowed to digest for several days with a large quantity of ether, again washed with ether, pressed, and re-crystallised from alcohol. The crystals are shaken with ether and hydrochloric acid, and the ethereal layer is agitated with ammonia and aqueous neutral acetate of lead. The upper of the two layers thus obtained contains oleate of lead in solution: this is decomposed by hydrochloric acid, and the oleic acid is converted into baryta-salt (Heintz).

*Properties.* Fine, dazzling white needles, which melt at 14° to a colourless oil. The fused substance solidifies at 4° to a white, hard crystalline mass, expanding considerably, so that the fluid portion is driven out. Sp. gr. 0·898 at 19° (Chevreul). Volatilises in a vacuum

without decomposition (Chevreul, Laurent). — Inodorous, tasteless. In the unchanged (not oxidised) condition, and also in alcoholic solution, its reaction is neutral (Gottlieb).

|  |  |  |  |  |  | Chevreul. |  | Laurent. |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | mean. |
| 36 C | ........ | 216 | ........ | 76·59 | ........ | 76.7 | ........ | 75·86 |
| 34 H | ........ | 34 | ........ | 12·06 | ........ | 11 4 | ........ | 12·28 |
| 4 O | ........ | 32 | ........ | 11·35 | ........ | 11·9 | ........ | 11·86 |
| $C^{36}H^{34}O^4$ | .... | 282 | ........ | 100·00 | ........ | 100·0 | ........ | 100·00 |

|  |  | Varrentrapp. |  |  |  | Gottlieb. |  | A. Völcker. |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | mean. |  |  |
| C | .... | 74·95 | ........ | 75·77 | ........ | 76·34 | ........ | 76·29 |
| H | .... | 11·74 | ........ | 12·06 | ........ | 12·14 | ........ | 12·14 |
| O | .... |  | ........ |  | ........ | 11·52 | ........ | 11·57 |
|  |  |  |  |  |  | 100·00 | ........ | 100·00 |

Gottlieb alone examined pure oleic acid; that of the other chemists was more or less oxidised and had an acid reaction. Laurent's acid was distilled in a vacuum: it did not solidify at 0°. — Earlier formulæ: $C^{35}H^{30}O^{3·5}$ (Chevreul); $C^{70}H^{68}O^7$ (Laurent); $C^{44}H^{40}O^5$ (Varrentrapp). — The oleic acid of butter, of almond oil, and of olive oil exhibits the same composition (Gottlieb). See also the analyses of the baryta-salt.

*Decompositions.* 1. Oleic acid, *heated* a few degrees above 100°, assumes a dark-brown colour, and before boiling evolves a large quantity of hydrocarbons, together with a little carbonic acid and water: at a comparatively low temperature, it yields a distillate of colourless oil (afterwards yellow, and at last brown, according to Chevreul), a little charcoal remaining behind (Bromeis). During the whole of the distillation, a tolerably regular evolution of carbonic acid and hydrocarbon gases takes place. The distillate deposits crystals of sebacic acid (xiv, 493) on cooling, the fluid portion consisting of a little undecomposed oleic acid and hydrocarbons boiling at 160—280° and higher. That portion of the distillate which passes over with the water-vapour contains 84·13 p. c. C., 13·02 H., and 2·85 O. (Varrentrapp). The distillate contains also acetic (Chevreul), caproic, caprylic, and probably butyric and valerianic acids. Pure oleic acid yields a large quantity, the oxidised acid only a small quantity of sebacic acid (Gottlieb), and hence Bromeis did not obtain any by the distillation of his butyroleic acid.

2. Oleic acid (which, in the solid state, is unalterable in the *air* (Gottlieb), absorbs, in the melted state, at 15°, in 14 days, 20 times its volume of oxygen without forming any perceptible amount of carbonic acid or water (Bromeis). After exposure to the air for five hours, at 100°, it is yellow and rancid, and solidifies only partially in the cold: it then contains, on an average, 73·23 p. c. C., 12·07 H., and 14·70 O., or 34 at. carbon, 33 at. hydrogen, and 5 at. oxygen (Gottlieb). An altered acid of similar composition (containing 72·5 to 73·7 p. c. C., and and 11·6 to 12·4 p. c. H.) was investigated by Bromeis as butyroleic acid. By the further action of oxygen, products are formed, which do not solidify at 14°, and prevent the crystallisation of the yet unchanged acid (Gottlieb). The oxidation-products are converted into the silver-salt and the ethyl-compound of oleic acid (see below);

but in preparing the baryta-salt, they remain in the mother-liquor, and are separated from it by mineral acids as a red-brown, rancid, very acid and viscid oil, the baryta-compounds of which contain 14·28 and 15·63 p. c. of baryta (Gottlieb). Concerning the formation of ozone in this oxidation, see Schönbein (*J. pr. Chem.* 74, 338).

3. Oleic acid *burns* when heated in the air (Chevreul).

4. Oleic acid, submitted to dry distillation with *sulphur*, yields a red-brown, disagreeably smelling oil [apparently containing odmyl (x, 97)], in which margaric acid is suspended; the reaction is attended with violent intumescence, and the evolution of a large quantity of hydrosulphuric acid. The distillate is free from sebacic acid (Anderson, *Phil. Mag. J.* 31, 164; *Ann. Pharm.* 63, 370). The margaric acid here spoken of may be palmitic acid (xvi, 356) (Kr.).

5. *Bromine* and *chlorine* form with oleic acid, in presence of water, bromoleic and chloroleic acids; *iodine* does not act upon it (Lefort).

6. *Nitrous acid* converts oleic acid into elaidic acid, without forming a second decomposition-product (Gottlieb). See under *Elaidic acid.*

7. In the decomposition of oleic acid by *nitric acid*, volatile acids of the general formula $C^nH^nO^4$, non-volatile acids of the formula $C^nH^{n-2}O^8$, azelaic acid, and other less accurately investigated products, are formed.

*a.* When oleic acid is cautiously added in small quantities to moderately hot red fuming nitric acid, a violent reaction takes place, and a large quantity of red vapours charged with *volatile acids*, is evolved. If, after the first action has ceased, the mixture is heated more strongly and then boiled for several days, with addition of more nitric acid if necessary, and the contents of the retort are at last freed from all volatile products by adding water and distilling, a distillate is obtained containing a mixture of the following acids, viz., in greatest quantity, caproic, valerianic, and acetic acids; in medium quantity, caprylic, butyric, and propionic acids; in smallest quantity, capric, pelargonic, and œnanthylic acids (Redtenbacher, *Ann. Pharm.* 59, 41).

When a weaker (commercial) acid is employed in the oxidation, for the sake of preparing the non-volatile products, the distillate possesses an irritating odour, which attacks the respiratory organs, and is not destroyed by neutralising with carbonate of soda. On distilling the solution (first rendered alkaline), a colourless, thin, volatile oil is obtained, but in too small quantity for further examination. (Bromeis, *Ann. Pharm.* 35, 93). Wirz (*Ann. Pharm.* 104, 261), who, however, oxidised the non-volatile acids of cocoa-nut oil with nitric acid, also mentions this volatile body, as well as an (acid?) oil of the distillate which he erroneously regarded as Laurent's azoleic acid or œnanthylic acid. The distillate obtained in the oxidation of fatty oil of almonds by nitric acid is also regarded by Arppe (*Ann. Pharm.* 120, 292) as œnanthylic acid (as found by experiment?).

*b.* Concentrated or weaker nitric acid, heated with oleic acid, in the proportion of 2 to 7 volumes of the former to 1 volume of the latter, reacts violently after an hour, so that a part of the liquid is projected from the vessel containing it; but on further heating, the oleic acid is quietly oxidised, becoming thinner and clearer, and at length disappearing completely. The *residual acid solution* contains succinic acid (x, 108) and, according to Laurent and Bromeis, lipic (x, 434), adipic (xi, 422), pimelic (xii, 463), suberic (xiii, 204), and azelaic (xvii, 79)

acids, and, according to Wirz (in the oxidation of the acids of cocoa-nut oil) also lepargylic (xiii, 374) acid. Arppe (*Ann. Pharm.* 95, 242 ; 115, 143), however, doubts the purity of most of the acids thus obtained ; he considers that the presence of lipric, adipic, and lepar-gylic acids is not established, and finds, as solid products of the oxida-tion of oleic acid (and other fats) only succinic, suberic, and azelaic acids, with perhaps a fourth uncrystallisable acid. Arppe formerly de-scribed, as a product of the oxidation of oleic acid, another acid, X, which he after-wards regarded as a secondary product of sublimation, and lately (*Ann. Pharm.* 124, 98) as pimelic acid. Sebacic acid, which is formed by the oxidation of spermaceti, is not produced by the action of nitric acid on oleic acid (Arppe).

The following products seem to be formed more especially by the incomplete oxidation of oleic acid. — I. *A solid fatty acid.* If, after the first violent action of nitric acid has ceased, the residue is cooled, it solidifies to a semi-solid mass, from which alcohol takes up margaric acid melting at 60° (containing 74·08 p. c. C., 12·50 H.). The margaric acid may, in this case, be formed from the impure oleic acid employed, but the pure acid, treated in the same way, also yields an acid melting at 80°, solidifying at 70°, and forming with potash a red soap from which acids precipitate a thick brown oil (Bromeis). — II. *Nitro-caprylic* and *Nitro-capric acids* (xiii, 217 and xiv, 500). These were obtained by Wirz in the oxidation of the acids of cocoa-nut oil, and appear to be mixed with the solid acid (I), since they are reddened by potash. The following product should also be mentioned here. When oleic acid is boiled with red fuming nitric acid (see above), not, however, till the fatty layer completely disappears, there floats upon the surface of the cooled liquid, an unctuous fat, heavier than water, and having the smell of perspiration ; it is easily soluble in alcohol and ether, and is precipitated from its blood-red alkaline solutions by acids without alteration. It explodes when heated, with an odour of cinnamon, evolving nitrous and volatile fatty acids, and leaving a black, tough residue which contains suberic acid. By boiling with water it is decomposed into fatty acids which volatilize, and suberic and pimelic acids which remain behind (Redten-bacher). — III. Laurent's *Azoleic Acid.* It is produced by boiling oleic acid with nitric acid, according to x, 434, till three-fourths is dissolved, and forms the oily layer which floats undissolved on the surface of the acid solution. When removed and distilled alone, it passes over at first undecomposed, then blackens and froths up, and towards the end of the distillation yields a sublimate consisting of a difficultly fusible, white powder. Azoleic acid, heated with alcohol and oil of vitriol, yields an ether, one-fifth of which distils unchanged, the remainder being decomposed in the same manner as the acid by further heating. When decomposed by alcoholic potash, with subsequent addition of hydrochloric acid, it yields azoleic acid insoluble in water, and containing 62·81 p. c. C., 10·71 H. (Laurent). According to Bromeis, (*Ann. Pharm.* 35, 109 ; 37, 300), who analysed the ether, this acid has the same composition as œnanthylic acid, and, according to Tilley (*Ann. Pharm.* 39, 166), is probably identical therewith. Œnanthylic acid, however, when obtained as the principal product of the oxidation of castor oil, passes over in the distillate, and, according to Redtenbacher, is obtained from oleic acid in very small quantity only, together with many other acids, whilst Laurent's azoleic acid is obtained from the residue. The formation of œnanthylic acid, here and above (by Arppe), seems to be merely conjectured and not established by experiment (Kr.).

8. Oleic acid, distilled with *bichromate of potash* and sulphuric acid, yields an acid distillate, which smells like tallow and rape-oil (Arzbächer, *Ann. Pharm.* 73, 199).

9. The brown mixture of *peroxide of lead* and oleic acid is discolour-ised at 120°, and becomes thick and viscid, evolving a large quantity of water-vapour, but no other gas (Bromeis, *Ann. Pharm.* 42, 71).

10. Oleic acid, mixed with *oil of vitriol*, forms Frémy's oleo-sul-phuric acid, an aqueous solution of which soon splits up into metoleic and hydroleic acids. See further under Olive-oil. — A single drop of oil of

vitriol colours oleic acid brown (Varrentrapp), especially when the acid is already partially decomposed (Gottlieb).

A solution of oleic acid in oil of vitriol, heated to 100°, evolves sulphurous acid, and perhaps also hydrosulphuric acid, with coloration, but without frothing ; above 100° it froths up violently and carbonises (Chevreul). The sulphuric acid solution behaves like ricinoleic acid on addition of sugar (Neukomm). When 3 drops of oleic acid are shaken up with 3 cubic centimetres of alcohol, and 1 drop of sugar solution is added, together with 4 or 5 drops of oil of vitriol, the mixture assumes a rose-to carmine-red colour from the bottom upwards, and when shaken after three hours becomes red-brown-violet, while part of the oleic acid collects on the surface (Benecke, *Studien über Gallenbestandtheile*, Giessen, 1862).

11. When melted with *hydrate of potash*, oleic acid splits up into palmitate and acetate, with evolution of hydrogen (Varrentrapp).

$$C^{36}H^{34}O^4 + 2(KO,HO) = C^{32}H^{31}KO^4 + C^4H^3KO^4 + 2H.$$
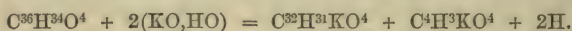
From the further action of the hydrate on the acetic acid, a little oxalic acid is produced (Varrentrapp). In the distillation with excess of hydrate of potash, an odour of butyrate of amyl is evolved (Al. Müller, *Handwörterbuch*, 6, 874).

12. Oleic acid, distilled with $\frac{1}{4}$th of its weight of *quick lime*, yields a liquid, neutral, unsaponifiable distillate, which deposits only traces of a solid body, and probably stands in the same relation to oleic acid as stearone to stearic acid. The residue contains carbonate of lime (Bussy, *Ann. Pharm.* 9, 271).

On distilling a mixture of 1,000 grammes of oleic acid, 300 gr. hydrate of lime, and 300 gr. soda-lime, and cooling the distillate, a liquid is obtained amounting to two-thirds of the quantity of the oleic acid employed. The non-condensable gases, absorbed by an excess of bromine, form bromine-compounds, from which, by agitation with caustic soda and washing with water, the bromides of the hydrocarbons $C^nH^n$ may be separated. In this way were obtained, from 3 kilogrammes of oleic acid, with the aid of an equal quantity of bromine, 100 gr. of bibromide of ethylene (viii, 366), 600 gr. of bibromide of propylene, $C^6H^6Br^2$, 100 gr. of bibromide of butylene, $C^8H^8Br^2$, 50 gr. of bibromide of amylene, $C^{10}H^{10}Br^2$, and 200 to 300 gr. of unseparated volatile bromine-compounds of hydrocarbons of higher atomic weight (Berthelot, *N. Ann. Chim. Phys.* 53, 200).

13. Oleic acid, heated with an equal quantity of *glycerin*, yields triolein, and, with an excess of glycerin, monolein. A mixture of oleic acid and glycerin, saturated, at 100° with hydrochloric acid gas, yields a neutral compound corresponding to triolein, but containing also hydrochloric acid. In the same manner, when oleic acid and glycerin are heated to 100° for 71 hours with tartaric, phosphoric, or sulphuric acid, the resulting glyceride contains a portion of the second acid in combination (Berthelot, *N. Ann. Chim. Phys.* 41, 248). See also xvi, 358.

*Combinations.* Oleic acid is insoluble in *water*.

It dissolves in 10 parts of cold *oil of vitriol* without decomposition, with slight evolution of heat, and coloration, which is increased to a certain extent after some days (Chevreul). See above.

*Oleates.*—Oleic acid decomposes the carbonates of the alkalis when heated therewith, slowly expelling the carbonic acid (Chevreul, Gottlieb). According to Unverdorben, it also partially decomposes acetate and hydrochlorate of lime. — The oleates are soft, frequently oily, or easily fusible to an oil, and more easily soluble in alcohol (and especially so in ether) than in water (Chevreul). Oleic acid easily forms acid and basic salts, and when an impure acid is employed, the impurities may be transferred to the salts in definite proportions (Gottlieb). See Oleate of silver.

*Soaps* are mixtures of salts, principally oleates, palmitates, and stearates. They are prepared, in some cases, by heating the base with a fatty body and water; in other cases (especially when the base is too feeble to effect saponification) by double decomposition. They are the harder the more palmitic and stearic acids, the softer the more oleic acid they contain; almond and olive oils, however, yield harder soaps than tallow, lard, or butter.

*Oleate of Ammonia.* — Oleic acid instantly combines with aqueous ammonia, with rise of temperature, forming a jelly which is completely soluble in water at 15°. The solution becomes cloudy on boiling, from loss of ammonia (Chevreul).

*Oleate of Potash.* — a. *Mono-salt.* Oleic acid combines with caustic potash, the combination being attended with evolution of heat. A solution of 47·2 parts of caustic potash dissolves 295 parts, or rather more than 1 atom, of oleic acid (Chevreul). — One part of oleic acid, heated with one part of caustic potash and five parts of water, forms a soft salt, which is insoluble in the supernatant liquid, and becomes harder on cooling. A mixture of 2 parts of oleic acid, 1 part of caustic potash, and 8 parts of water, yields a pellucid jelly, which separates from the aqueous liquid when heated with $\frac{1}{2}$ part of caustic potash. If this be pressed and dissolved in boiling alcohol, and the solution allowed to evaporate spontaneously, the salt is left in the form of a transparent jelly. — In the voltaic circuit it liberates oleic acid at the positive, and potash at the negative pole. It is decomposed by acids, even by carbonic acid, when passed through the solution at a temperature of 5°. — Exposed to air saturated with moisture, at 12°, it takes up, in seven days, 162 parts of water, and deliquesces. Swells up to a transparent jelly in 2 parts of cold water, and dissolves completely in 4 parts to a ropy syrup. The solution in a very large quantity of water deposits binoleate of potash when kept for some months, potash and a trace of oleic acid remaining in solution. Oleate of potash dissolves in 2·15 parts of alcohol at 10°, and in 1 part of alcohol of sp. gr. 0·821 at 50°. The solution turns cloudy at 40·5°, congeals to a soft mass at 31°, and solidifies at 12°. A solution in 2 parts of hot alcohol remains clear down to 12°, and deposits crystals of the mono-acid salt at 10°. Dissolves in 29·1 parts of boiling ether, the solution remaining clear at 12°. Insoluble in concentrated solution of caustic potash, and in various aqueous salts, *e.g.*, chloride of sodium (Chevreul).

|  |  |  |  |  |  | Chevreul. | | |
|  |  |  |  |  |  | earlier. |  | later. |
|---|---|---|---|---|---|---|---|---|
| $C^{36}H^{33}O^3$ | ........ | 273 | ........ | 85·26 | ........ | 86·35 | ........ | 84·81 |
| KO | ........ | 47·2 | ........ | 14·74 | ........ | 13·65 | ........ | 15·19 |
| $C^{36}H^{33}KO^4$ | .... | 320·2 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

*b. Bi-acid.* — On heating 11·2 parts of oleic acid with 1 part of hydrate of potash and 43·4 parts of water, and afterwards diluting the whole with 108 parts of water, a jelly is obtained, the filtrate from which contains a small quantity of potash, and probably a trace of acid. The jelly is insoluble in water, but soluble in hot and cold alcohol. It reddens litmus, the colour disappearing on washing with water (Chevreul).

*Potash* forms softer *soaps* with the fats than soda ; with lard it yields a soap of the consistence of butter, containing, after pressing, 14·9 p. c. potash, 66·1 p. c. saponified fat, and 19·0 p. c. water, and after pressing more strongly, 15·85 p. c. potash, 72·4 fat, and 11·75 water (Chevreul). Potash-soap is soluble in water and alcohol. It is precipitated from its aqueous solution by common salt [not by salts of potash (Wittstein, *Pharm. Viertelj.* 1,426)].

*Oleate of Soda.* — *Mono-acid salt.* — The union of oleic acid and moist hydrate of soda is attended with rise of temperature. Water containing 31·3 pts. of soda dissolves 310 pts. of oleic acid. — One part of oleic acid, heated with $\frac{2}{3}$ part of hydrate of soda, and 5 parts of water, yields a soft jelly, insoluble in the alkaline liquid, solidifying on cooling to a tenacious mass. On boiling 1 part of oleic acid with $\frac{1}{2}$ part of hydrate of soda and 8 parts of water, the salt is deposited in translucent granules, which are opaque when cold. When boiled with an additional 4 parts of water, it separates from the alkaline liquid in the form of a jelly. If this jelly be dried and dissolved in hot alcohol, and the solution allowed to evaporate spontaneously, there remains a solid, brittle, transparent mass, having a bitter alkaline taste (Chevreul). The salt crystallises from absolute alcohol, but not from alcohol containing water, nor from a solution so concentrated as to be syrupy (Varrentrapp). Exposed to moist air, 1 part of the salt takes up, in six days, 0·975 pts. of water without deliquescing. Dissolves very easily in 10 pts. of water at 12°, in 20·6 pts. of alcohol of sp. gr. 0·821 at 13°, in 10 pts. at 32°, and in 100 pts. of boiling ether, a portion being deposited on cooling (Chevreul).

|  |  |  |  |  |  | Chevreul. | | |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | earlier. |  | later. |
| $C^{36}H^{33}O^{3}$ | ............ | 273 | ........ | 89·8 | ........ | 90·8 | ........ | 89·39 |
| NaO | ............ | 31 | ........ | 10·2 | ........ | 9·2 | ........ | 10·61 |
| $C^{36}H^{33}NaO^{4}$ | ... | 304 | ........ | 100·0 | ........ | 100·0 | ........ | 100·00 |

*Soda-soap* is prepared either from fat and soda, or from potash and fat with subsequent addition of common salt. In the latter case the chloride of sodium and the potash-soap are partially converted into chloride of potassium and soda-soap, the latter rising to the surface of the ley, while the excess of potash or soda remains in solution, together with other salts accidentally present and glycerin. The soap is capable of taking up a large quantity of water without losing its solidity. The soda-soaps of commerce contain, as a rule, from 14 to 38 p. c. of water, the proportion varying, however, in particular cases, between 8 and 75 p. c. — — It dissolves easily in warm water and in alcohol. The solutions solidify on cooling, the more easily the greater the quantity of stearic acid present. They are decomposed by nearly all acids, and by salts of the earths and heavy metals. Soaps are completely separated from their solutions by common salt and sal-ammoniac.

*Oleate of Baryta.* — a. *Mono-acid salt.* — Preparation see above. It may also be obtained by precipitating the soda-salt with chloride of barium, or by boiling oleic acid with baryta-water or carbonate of baryta (Chevreul, Varrentrapp). — Dazzling white, loose, finely crystallised powder, which cakes together at 100° without melting (Gottlieb). More easily fusible when impure. Tasteless, insoluble in water, but soluble in boiling alcohol. One litre of a boiling alcoholic solution deposits 5 grammes of the salt on cooling (Berthelot).

|  |  |  |  |  | Varrentrapp. *mean.* |  | Gottlieb. *mean.* |  | Völcker. |
|---|---|---|---|---|---|---|---|---|---|
| 36 C | 216 | .... | 61·79 | .... | 63·36 | .... | 61·51 | .... | 61·59 |
| 33 H | 33 | .... | 9·44 | .... | 9·51 | .... | 9·44 | .... | 9·46 |
| 3 O | 24 | .... | 6·87 | .... | 8·79 | .... | 7·13 | .... | 7·03 |
| BaO | 76·5 | .... | 21·90 | .... | 18·34 | .... | 21·92 | .... | 21·92 |
| $C^{36}H^{33}BaO^4$ | 349·5 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 |

| | Maskelyne. | | *a.* | | Heintz. *b.* | | *c.* | | Gössmann. |
|---|---|---|---|---|---|---|---|---|---|
| C | 61·80 | ........ | 61·20 | ........ | 61·65 | ........ | 61·53 | ........ | 61·68 |
| H | 9·64 | ........ | 9·45 | ........ | 9·44 | ........ | 9·45 | ........ | 9·46 |
| O | 6·68 | ........ | 7·45 | ........ | 6·94 | ........ | 7·05 | ........ | 6·40 |
| BaO | 21·88 | ........ | 21·90 | ........ | 21·97 | ........ | 21·97 | ........ | 22·46 |
| | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Chevreul found in his earlier analyses 21·88 p. c., afterwards 22·97 p.c., BaO. Varrentrapp's baryta-salt contained impure (oxidised) oleic acid (Gottlieb). Völcker's acid (*Ann. Pharm.* 64, 345) was obtained from oil of ben; Maskelyne's (*Chem. Soc. Q. J.* 8, 1) from vegetable tallow; Heintz's from (*a*) beef-suet, (*b*) mutton-suet, (*c*) butter; Gössmann's from cantharides' fat.

b. *Bi-acid?*—The mono-acid salt dissolves abundantly in moderately warm oleic acid (Chevreul). — A dilute alcoholic solution of *a* deposits, on cooling, flocks containing, after drying first in a vacuum, and afterwards at 60° to 70°, 10·30 p. c. of baryta; the mother-liquor yields crystals of the mono-acid salt when concentrated (Gössman, *Ann. Pharm.* 86, 322).

|  |  |  |  | Gössmann. |
|---|---|---|---|---|
| $C^{72}H^{67}O^7$ | 555 | ........ | 87·88 | |
| BaO | 76·5 | ........ | 12·12 | ........ 10·30 |
| $C^{36}H^{33}BaO^4,C^{36}H^{34}O^4$ | 631·5 | ........ | 100·00 | ........ |

*Oleate of Strontia.* — Obtained by boiling oleic acid with carbonate of strontia. Resembles the baryta-salt. Soluble in alcohol (Chevreul).

|  |  |  |  | Chevreul. |
|---|---|---|---|---|
| $C^{36}H^{33}O^3$ | 273 | ........ | 84· | |
| SrO | 52 | ........ | 16· | ........ 15·92 to 16·2 |
| $C^{36}H^{30}SrO^4$ | 325 | ........ | 100· | |

*Oleate of Lime.* — Oleate of potash precipitates from chloride of calcium a white powder, which melts at a gentle heat and becomes transparent (Chevreul). Dissolves in alcohol and ether.

| | | | | |
|---|---|---|---|---|
| $C^{36}H^{33}O^3$ .............. | 273 | ........ | 90·7 | |
| CaO ... ............ | 28 | ........ | 9·3 | ........ 8·8 |
| $C^{36}H^{33}CaO^4$ ............ | 301 | ........ | 100·0 | |

*Oleate of Magnesia.* — Obtained by precipitating a boiling solution of sulphate of magnesia with oleate of potash. — White, somewhat translucent granules, softening between the fingers (Chevreul).

| | | | | |
|---|---|---|---|---|
| $C^{36}H^{33}O^3$ ................ | 273 | ........ | 93·18 | |
| MgO ................ | 20 | ........ | 6·82 | ........ 7·0 |
| $C^{36}H^{33}MgO^4$ ........ | 293 | ........ | 100·00 | |

*Oleate of Chromium.* — Precipitated by oleate of potash from a solution of chloride of chromium. Violet precipitate, soft in the moist state, hard when dried (Chevreul).

*Oleate of Zinc.* — Precipitated from sulphate of zinc by a boiling solution of oleate of potash. — White. Melts under 100° (Chevreul).

| | | | | |
|---|---|---|---|---|
| $C^{36}H^{33}O^3$ ............ | 273 | .... ... | 87·09 | |
| ZnO ................ | 40·5 | ........ | 12·91 | ........ 12·91 |
| $C^{36}H^{33}ZnO^4$ ........ | 313·5 | ........ | 100·00 | |

*Oleate of Lead.* — Aqueous solutions of soap are completely precipitated by oxide of lead, no oleic (or margaric) acid remaining in solution (Gobley, *N. J. Pharm.* 21, 248). — Dissolves in ether (Gusserow).

a. *Basic.* — Obtained by boiling oleic acid with an excess of basic acetate of lead. Soft at 20° ; melts completely to a transparent liquid at 100° (Chevreul).

| | | | | |
|---|---|---|---|---|
| $C^{36}H^{33}O^3$ .................... | 273 | ........ | 54·93 | |
| 2 PbO ................ | 224 | ........ | 45·07 | ........ 45·18 to 45·95 |
| $C^{36}H^{33}PbO^4,PbO$ .... | 497 | ........ | 100·00 | |

b. *Mono-salt.* — A cold alcoholic solution of oleate of soda is precipitated with neutral acetate of lead, and the flocculent precipitate is washed and dried in a vacuum (Gottlieb). — Light, loose, white powder, which melts to an oil about 80°, and solidifies on cooling to a brittle translucent mass (Gottlieb).

| | | | | |
|---|---|---|---|---|
| 36 C ........................ | 216 | ........ | 56·16 | ........ 55·88 |
| 33 H ........................ | 33 | ........ | 8·58 | ........ 8·69 |
| 3 O ........................ | 24 | ........ | 6·25 | ........ 6·48 |
| PbO .................... | 112 | ........ | 29·01 | ........ 28·95 |
| $C^{36}H^{33}PbO^4$ ............ | 385 | ........ | 100·00 | ........ 100·00 |

*Oleate of Iron.* — Dissolves in all proportions in alcohol, forming brown solutions. The solution in a small quantity of alcohol is oily (Unverdorben).

*Oleate of Cobalt.* — Oleate of potash throws down from hot sulphate of cobalt a precipitate at first bluish-green, afterwards green, which settles down slowly (Chevreul).

*Oleate of Nickel.* — Greenish-yellow precipitate, which is very slowly deposited (Chevreul).

*Oleate of Copper.* — Obtained by precipitating a boiling solution of sulphate of copper with oleate of potash, or by heating oleic acid with oxide of copper. — Splendid green salt perfectly fluid at 100° (Chevreul). — Dissolves in alcohol in all proportions, with blue-green colour; in a small quantity it forms an oily liquid (Unverdorben). Concerning its action on the organism, see Langenbeck and Städeler (*Ann. Pharm.* 97, 155).

|  |  |  |  |  | Chevreul. |
|---|---|---|---|---|---|
| $C^{36}H^{33}O^3$ | .... ...... | 273 | ........ | 87·22 | |
| CuO | ............ | 40 | ........ | 12·78 | ........ 12·23 |
| $C^{36}H^{33}CuO^4$ | ........ | 313 | ........ | 100·00 | |

*Oleates of Mercury.* — a. *Mercurous Salt.* — Oleic acid is digested for some time with mercurous oxide; or mercurous nitrate is precipitated with oleate of potash. — Whitish-grey flocks, bluish after drying. — Forms with ammonia a black ammoniacal powder. — Insoluble in water and cold alcohol, but soluble in hot alcohol. Soluble in hot and cold ether (Harff, *N. Br. Arch.* 5, 306).

|  |  |  |  |  | Harff. |
|---|---|---|---|---|---|
| $C^{36}H^{33}O^3$ | .................. | 273 | ........ | 56·76 | |
| $Hg^2O$ | .................. | 208 | ........ | 43·24 | ........ 43·20 |
| $C^{36}H^{33}Hg^2O^4$ | ............ | 481 | ........ | 100·00 | |

*Mercuric Salt.* — Oleate of potash throws down from mercuric nitrate, white flocks which turn greasy on washing and dry up to a solid mass. Contains 30·18 p. c. of oxide of mercury (1 at. = 28·35 p. c. HgO). Dissolves slightly in cold, better in hot alcohol, and with moderate facility in ether (Harff).

*Oleate of Silver.* Nitrate of silver forms with the soda-salt a white, very bulky precipitate, which easily blackens from reduction of silver (Gottlieb). The precipitate turns brown on exposure to light, and when dried in a vacuum at a temperature considerably below 100°; it is converted into a soft, pasty mass, which dries with difficulty (Varrentrapp). Gottlieb added to an alcoholic solution of partially oxidised oleic acid, first a little ammonia, then an excess of nitrate of silver, and obtained thereby a precipitate of loose flocks, which afterwards united into a soft, yellowish-white mass. It contained 66·82 p. c. C., 10·43 H., and 11·71 AgO., corresponding to the formula $C^{108}H^{98}AgO^{15}$, or the ter-acid salt of an altered oleic acid (Gottlieb).

Oleic acid mixes with cold and hot *alcohol* in all proportions : from a mixture of equal parts of acid and alcohol, water does not take up any alcohol (Chevreul). — It is miscible also with *ether* (Chevreul). It is dissolved by *bile*, forming therewith a soap having a strongly acid reaction (Marcet, *Phil. Mag. J.* 17, 145).

Oleic acid mixes with *margaric* and *stearic acids* in all proportions. Cold alcohol takes up from such mixtures a large quantity of oleic, together with a little stearic and margaric acids. Alcohol at a temperature of 60° dissolves the whole of the mixture, but deposits the greater part of the stearic and margaric acids on cooling (Chevreul).

TABLE of the melting-points of mixtures of Oleic and Margaric acids, according to Chevreul.

| Percentage of oleic acid. | Melting point. | Percentage of oleic acid. | Melting point. | Percentage of oleic acid. | Melting point. |
|---|---|---|---|---|---|
| 95 | 7° | 60 | 41° | 25 | 49·25° |
| 90 | 17 | 55 | 42·5 | 20 | 50·25 |
| 85 | 26·5 | 50 | 44 | 15 | 51·5 |
| 80 | 31·5 | 45 | 45·75 | 10 | 53 |
| 75 | 35·5 | 40 | 46·75 | 5 | 54 |
| 70 | 37·5 | 35 | 48 | 1 | 55 |
| 65 | 39·5 | 30 | 48·5 | | |

### Acids nearly identical with Oleic Acid.

1. Walter's *Moringic Acid.* Occurs in oil of ben. See below. Colourless or yellowish oil of sp. gr. 0·908 at 12·5°. Congeals to a crystalline mass at 0°. Has a faint odour and an insipid taste. Reddens litmus. Assumes a blood-red colour with oil of vitriol, and carbonises when heated therewith. Contains 74·9 p. c. C., 11·8 H., and 13·3 O., corresponding to Walter's formula $C^{30}H^{28}O^4$, and likewise very nearly with that of oleic acid (*Compt. rend.* 22, 1143; *Ann. Pharm.* 60, 271).

2. *Filixoleic acid.* Occurs, according to Luck, in the roots of *Aspidium Filix mas.* When from an ethereal extract of the root, the filicic acid is removed in the manner already described (xvi, 126), an ethereal solution of the oil of the root is obtained, and from this the oleic acid is separated. Purified by Gottlieb's method (p. 63), it forms a bright-yellow, inodorous oil, which has a faint taste and strongly acid reaction, and does not solidify at 8°. It contains 75·06 p. c. C., 12·58 H., and 12·36 O., and has therefore the composition of oleic acid. It yields the same products as oleic acid when submitted to dry distillation, and forms a baryta-salt containing 62·51 p. c. C., 9·96 H., 8·35 O., and 19·18 BaO. Luck proposed the formula $C^{42}H^{41}O^8$ (*Jahrb. pr. Pharm.* 22, 153).

### Elaïdic Acid.

$$C^{36}H^{34}O^4 = C^{36}H^{34},O^4.$$
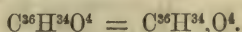
Literature, History, and Formation also of Elaïdin.

POUTET.   *J. Pharm.* 5, 337; 6, 77; *Ann. Chim. Phys.* 12, 58.

F. BOUDET.   *J. Chim. méd.* 8, 641; *Ann. Chim. Phys.* 50, 391; *J. Pharm.* 18, 469; *Ann. Pharm.* 4, 1; *Schw.* 66, 186.

LAURENT.   *Ann. Chim. Phys.* 65, 152; *J. pr. Chem.* 12, 411. — *Rev. scient.* 14, 569.

H. MEYER.   *Ann. Pharm.* 35, 174.

GOTTLIEB.   *Ann. Pharm.* 57, 52.

Poutet discovered that olive oil has the property of solidifying with

mercurous nitrate. This property was more accurately investigated by Boudet, and especially by Gottlieb, the former of whom discovered elaïdic acid. — The statement of Pelouze and Boudet that cocoa-nut oil contains elaïdin, and that of Boudet that margarin may be converted into elaïdin, have been found to be erroneous.

*Formation.* The non-drying fatty oils, in contact with hyponitric acid, solidify to elaïdin (Boudet). Oleic acid, under the same circumstances, is converted into elaïdic acid (Pelouze & Boudet; Meyer), no second product being formed when pure oleic acid is used (Gottlieb).

Olive oil with $\frac{1}{12}$th of a solution of 6 parts of mercury in 7 parts of nitric acid of sp. gr. 1·35 forms a mixture which solidifies in two hours in winter and in eight hours in summer, whilst poppy oil, treated in the same way, remains quite fluid, throwing down only a slight precipitate (Poutet). In this reaction hyponitric acid is the only active agent, a very small quantity of it sufficing to effect the conversion. Olive oil placed in contact with 200 vols. of nitric acid and 100 vols. of oxygen absorbs the gases completely, turning green and becoming nearly solid within two hours (Boudet). Oleic acid behaves in the same manner (Gottlieb).

Olive oil solidifies with $\frac{1}{33}$rd of hyponitric acid (dissolved in 3 times its weight of nitric acid of sp. gr. 1·35) in 70 minutes, with $\frac{1}{50}$th in 78, with $\frac{1}{75}$th in 84, with $\frac{1}{100}$th in 130 minutes, and with $\frac{1}{200}$th in $7\frac{1}{4}$ hours; $\frac{1}{400}$th does not cause it to solidify. The product has the same properties whatever quantity of hyponitric acid has been employed. — Other fatty oils (but not the drying oils of hemp, linseed, walnut, poppy, and beech-nut) are rendered thick by hyponitric acid. One hundred parts of the undermentioned fatty oils at 17°, added to a solution of 3 pts. of hyponitric acid in 9 pts. of nitric acid solidify in the following times :—

| Oil of cashew-nut in | 43 | minutes, to a | sulphur-yellow | mass |
|---|---|---|---|---|
| Olive oil | ,, 73 ,, | ,, | blue-green | ,, |
| Hazel-nut oil | ,, 103 ,, | ,, | blue-green | ,, |
| Sweet almond oil | ,, 160 ,, | ,, | dirty-white | ,, |
| Bitter almond oil | ,, 160 ,, | ,, | dark-green | ,, |
| Rape oil | ,, 2400 ,, | ,, | brown-yellow | ,, |

Olive oil, mixed with $\frac{1}{4}$th or more of hyponitric acid, froths up and becomes heated, turning green and ropy; it does not solidify but is capable, when mixed with 5 or 6 times the quantity of olive oil, of converting the whole into elaïdin (Boudet). — When elaïdic acid is melted with dilute nitric acid and copper turnings, with access of air, the nitrous acid formed is taken up by the fluid elaïdic acid, which is thereby converted into a colourless, heavy, viscid oil. This oil, after being completely freed from nitric acid by washing with water, possesses the property of converting 20 times its volume of oleic acid into elaïdic acid in eight or ten days (Gottlieb). Impure elaïdin, formed by the action of mercurous or hyponitric acid on olive oil, gives off no gas in the cold; at a temperature of 100° it evolves a volume of nitrogen equal to that of the oil employed, and when heated for several hours, also carbonic acid (Boudet). Oleic acid also forms impure elaïdic acid, which, after absorbing 20 or 30 volumes of hyponitric acid, evolves only a small quantity of nitrogen, and no other gas, when

heated, the mass nevertheless containing nitrate of ammonia. The newly-formed product, heated with hydrate of lime, yields ammonia and a small quantity of neutral, odorous oil, insoluble in water (Gottlieb).

When olive oil, or oleic acid which has been changed by exposure to the air, is used in the preparation of elaïdic acid, there remains in the mother-liquor a red oil, which dissolves with red colour in alkalis, and is separated again by acids (Meyer). With pure oleic acid this body is not formed (Gottlieb).—The addition of poppy oil, even of 1 per cent. only, to olive oil retards the formation of elaïdin (Boudet). Almond oil mixed with drying fat no longer solidifies with nitrous acid (Schlippe, *Ann. Pharm.* 105, 19).

*Preparation.* Nitrous acid is passed into oleic acid for five minutes, and the liquid is cooled, whereupon it solidifies in half an hour to a yellow foliated mass. This mass is washed repeatedly with boiling water and afterwards dissolved in an equal weight of alcohol, and the crystals which form on standing are purified by re-crystallisation (Meyer). The acid obtained by saponifying elaïdin and decomposing the soap, cannot be purified by crystallisation from alcohol (Meyer).

*Properties.* Fine pearly laminæ, resembling boracic or benzoic acid (Boudet, Meyer), attaining a length of 2 inches, and a breadth of half an inch with angles of 112° and 68° (Laurent). Melts at 44° (Boudet), 44° to 45° (Meyer), and solidifies at 42° (Laurent), expanding considerably (Gottlieb). By partial solidification, pearly, translucent laminæ are obtained (Laurent). Distils almost unaltered. Has a strongly acid reaction.

| | | | Laurent. mean. | | Meyer. | Gottlieb. |
| | | | earlier. | later. | mean. | mean. |
|---|---|---|---|---|---|---|
| 36 C ............ | 216 | .... | 76·59 .... | 75·00 .... | 76·48 .... | 76·51 .... | 76·50 |
| 34 H ............ | 34 | .... | 12·06 .... | 12·27 .... | 12·07 .... | 12·25 .... | 12·18 |
| 4 O ............ | 32 | .... | 11·35 .... | 12·73 .... | 11·45 .... | 11·24 .... | 11·32 |
| $C^{36}H^{34}O^4$ | 282 | .... | 100·00 .... | 100·00 .... | 100·00 .... | 100·00 .... | 100·00 |

The above formula is according to Laurent (*Rev. Scient.*, 14, 569) and Gottlieb.— Isomeric with oleic acid (Gottlieb, Gerhardt, *Compt. rend.* 23, 1115). Earlier formulæ: $C^{70}H^{68}O^8$ (Laurent), $C^{72}H^{68}O^7$ (Meyer.)

*Decompositions.* 1. When elaïdic acid is subjected to *dry distillation* a portion is decomposed, with formation of hydrocarbons (Meyer). From impure elaïdic acid Meyer obtained also sebacic acid, the production of which by the dry distillation of the pure acid remained doubtful. No caprylic or capric acid is formed, as in the dry distillation of oleic acid (Gottlieb). 2. Melted elaïdic acid absorbs *oxygen.* After exposure to the air for some hours, at 100°, it solidifies only partially on cooling, so that an oil may be expressed from the solid portion. When it is maintained at a temperature of 65° for 14 days, the melting-point gradually sinks; the acid evaporates partially in oily drops, turns rancid, and is at last converted into a yellow viscid mass, having the smell of poppy oil, no longer solidifying with nitrous acid, and drying up on glass plates. It then contains 69·22 p. c. C., 10·58 H., and 20·20 O., or 36 at. C., 33 at. H., and 8 at. O. (Gottlieb). 3. Elaïdic acid melted with *hydrate of potash*, splits up like oleic acid into palmitic and acetic acids (Varrentrapp, Meyer).

*Combinations.* Elaïdic acid is insoluble in *water*. The acid expels carbonic acid from alkaline *carbonates*, and forms transparent, very thick soaps (Boudet, Meyer).

*Ammonia-salt.* — Soluble in water and alcohol.

*Potash-salt.* — Light, shining needles, soluble in water and alcohol (Boudet).

*Soda-salt.* A. *Mono-acid.* — Elaïdic acid is boiled with water and an excess of carbonate of soda; the solution is evaporated, and the residue exhausted with alcohol (Boudet). — Light, silvery laminæ, easily soluble in warm water and alcohol, less soluble in warm ether (Boudet, Meyer).

|  |  |  |  | Meyer. mean. |
|---|---|---|---|---|
| $C^{36}H^{33}O^3$ ............ | 273 | ........ | 89·8 |  |
| NaO ................ | 31 | ........ | 10·2 | ........ 10·41 |
| $C^{36}H^{33}NaO^4$ ........ | 304 | ........ | 100·0 |  |

B. *Bi-acid.* — A dilute aqueous solution of A becomes alkaline and turbid on standing, from separation of crystalline scales of a bi-acid salt (Boudet). Contains 5·17 p. c. NaO, and solidifies to a crystalline mass after melting (Laurent).

|  |  |  |  | Laurent. |
|---|---|---|---|---|
| $C^{72}H^{67}O^7$ ........................... | 555 | ........ | 94·71 |  |
| NaO ............................... | 31 | ........ | 5·29 | ........ 5·17 |
| $C^{36}H^{33}NaO^4,C^{36}H^{34}O^4$ ........ | 586 | ........ | 100·00 |  |

*Baryta-salt.* —White precipitate, containing 21·52 p. c. baryta (Meyer).

|  |  |  |  | Meyer. |
|---|---|---|---|---|
| $C^{36}H^{33}O^3$ ................ | 273 | ........ | 78·10 |  |
| BaO .................... | 76·5 | ........ | 21·90 | ........ 21·52 |
| $C^{26}H^{33}BaO^4$ ............ | 349·5 | ........ | 100·00 |  |

The *magnesia-salt* dissolves very slightly in water and alcohol (Boudet).

*Lead-salt.* — The acid loses 3·36 p. c. of water when heated with oxide of lead (Laurent) (1 at. = 3·19 p. c.). White, bulky precipitate, thrown down from the soda-salt by neutral acetate of lead acidified with acetic acid (Meyer). Dissolves slightly in alcohol.

|  |  |  |  | Meyer. mean. |
|---|---|---|---|---|
| $C^{36}H^{33}O^3$ .................... | 273 | ........ | 70·99 |  |
| PbO .................... | 112 | ........ | 29·01 | ........ 29·04 |
| $C^{36}H^{33}PbO^4$ ............ | 385 | ........ | 100·00 |  |

*Silver-salt.* — Obtained by precipitating an alcoholic solution of the soda-salt with nitrate of silver. White, bulky precipitate, difficultly soluble, after drying, in water, alcohol, and ether; more easily soluble in the moist state. Crystallizes from a solution in ammonia in small, white prisms (Meyer).

| | | | | | Meyer. *mean.* | | Gottlieb. *mean.* |
|---|---|---|---|---|---|---|---|
| 36 C | .................... | 216 | ........ | 55·51 | ........ 55·34 | ........ | 55·34 |
| 33 H | ............··..... | 33 | ........ | 8·49 | ........ 8·65 | ........ | 8·51 |
| 3 O | .................... | 24 | ........ | 6·16 | ........ 6·13 | ........ | 6·46 |
| AgO | ............·...... | 116 | ....·... | 29·84 | ........ 29·88 | ........ | 29·69 |
| C³⁶H³³AgO⁴ | ........ | 389 | ........ | 100·00 | ........ 100·00 | ........ | 100·00 |

Boudet found 29·81 p. c. AgO.

Elaïdic acid is very easily soluble in *alcohol*. Boiling alcohol dissolves it in all proportions : one part of alcohol of sp. gr. 0·92 at 36° dissolves 5 parts of the acid (Boudet). It is soluble in all proportions in alcohol, less freely soluble in *ether* (Meyer). A mixture of equal parts of elaïdic and *margaric* acids solidifies to a porcelain-like, translucent mass after melting; a mixture of 2 parts of elaïdic acid and 1 part of margaric acid melts at 42°, and solidifies in the crystalline state, like pure elaïdic acid (Gottlieb).

## Stearidic Acid.

$$C^{36}H^{34}O^4 \ = \ C^{36}H^{34}, O^4.$$
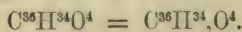
OUDEMANNS. *J. pr. Chem.* 89, 193.

Not named by Oudemanns.

*Formation.* By heating bromo-stearate of silver with water.

$$C^{36}BrH^{34}AgO^4 = C^{36}H^{34}O^4 + AgBr.$$
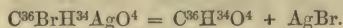
Bromostearate of silver is boiled with water for several hours ; the mixture of bromide of silver and stearidic acid, which separates, is treated with alcohol ; and the solution is filtered from bromide of silver and evaporated, with the addition of water. The lard-like residue, when submitted to distillation, yields colourless stearidic acid, whilst bromostearidic acid (formed from admixed bibromostearate of silver) remains behind, and is decomposed at a stronger heat.

*Properties.* Amorphous mass, resembling the soft animal fats. Melts at 35°, and has a peculiar faint odour. Distils unchanged.

| | | | at 100° | | Oudemanns. *mean.* |
|---|---|---|---|---|---|
| 36 C | ............... | 216 | ........ | 76·60 | ........ 76·16 |
| 34 H | ............... | 34 | ........ | 12·06 | ........ 11·99 |
| 4 O | ............... | 32 | ........ | 11·34 | ........ 11·85 |
| C³⁶H³⁴O⁴ | ............ | 282 | ........ | 100·00 | ......... 100·00 |

Isomeric with oleic and elaïdic acids.

With the *alkalis* it forms soaps, an alcoholic solution of which precipitates salts of the metals. Dissolves in *alcohol* more easily than elaïdic acid, and does not crystallise from the solution.

*Appendix to Oleic Acid and Supplement to* xiii, 374.

## Azelaic Acid.

LAURENT. *Ann. Chim. Phys.* 66, 156.
WIRZ. *Ann. Pharm.* 104, 270.
ARPPE. *Ann. Pharm.* 115, 143; 120, 288; 124, 86.

*Apelaic acid* (Berzelius). *Azelic acid* (Arppe).

Discovered by Laurent, and prepared pure by Arppe. Bromeis (*Ann. Pharm.* 35, 103) doubted the peculiarity of the acid. The acid described at xiii, 374, as *anchoic* or *lepargylic acid* is to be regarded as impure azelaic acid (Arppe).

*Formation.* Produced, together with other acids, by the oxidation of oleic acid by nitric acid (p. 66) (Laurent).
Obtained in small quantity from oleic acid, in greater quantity from almond oil, and most abundantly from ricinoleic acid, but not from spermaceti, bees'-wax, or stearic acid (Arppe). — Also from the fatty acids of cocoa-nut oil, and from Chinese wax, since these substances serve for the preparation of lepargylic acid.

*Preparation.* 1. Oleic acid is oxidised with nitric acid, according to x, 434, and the mixture of suberic and azelaic acids, which crystallises on cooling, is separated, according to xiii, 205, by treatment with ether, which takes up the azelaic and, at the same time, a portion of the suberic acid. The residue which remains on evaporation of the ether is again digested with so much cold ether that only one-half is dissolved, and the first half of the acid deposited from this solution is removed, only the half remaining in solution being considered pure (Laurent).

2. One or two pounds of castor oil are heated in a capacious retort with a little nitric acid of sp. gr. 1·25, and when the frothing which first takes place has subsided, more acid is added to the amount of 2 parts of acid to 1 part of oil. The whole is then boiled for a day, the acid solution is separated from the oil, and the latter is again boiled with fresh acid. In this way is obtained a distillate containing œnanthylic acid, and an acid solution with an oil floating on the surface; this last is removed by means of a tap-funnel.
*a.* The floating oil just mentioned, as well as that separated at a later stage of the process, is boiled with water, when azelaic acid is taken up by the water, and œnanthylic acid is volatilised with the aqueous vapour.
*b.* The acid solution is concentrated, with frequent addition of water, to drive off nitric acid, until it solidifies almost completely to a white granular mass, the oil which separates being removed. The granular mass, when washed on a filter with cold water, is resolved into an easily soluble portion, containing principally oxalic acid, and a more difficultly soluble mixture of acids, which, for the more complete separation of oxalic acid and oil, is once crystallised from warm water. The crystals are washed with cold water, dried, and melted,

and the mass, after solidifying, is triturated, and again washed with water, to remove more completely the easily soluble acids. The undissolved portion, again dried, melted, and rubbed to a fine powder, is repeatedly treated with twice its volume of ether, by which it is separated into azelaic acid which dissolves, and insoluble suberic acid. The ethereal solution is evaporated; the azelaic acid, which remains in the form of an oil, is dissolved in boiling water; and the crystals formed are removed before the mother-liquor is quite cold. The liquid afterwards throws down a granular deposit, consisting of a mixture of suberic and azelaic acids, from which ether takes up the latter acid. Azelaic acid thus obtained still contains an admixture of oil, from which it is freed by treating it with a quantity of ether insufficient for complete solution, dissolving the acid taken up in water, and removing the oily drops which separate by filtration. The acid is to be considered pure only when its melting-point is constant, and when its solution in warm water does not become turbid on cooling (Arppe).

*Properties.* Large, dazzling-white, pearly laminæ, or transparent flattened needles, having a glassy lustre. The faces are frequently curved. The crystals are distinctly cleavable in two directions at right angles to each other. From very dilute solutions they are deposited on cooling in laminæ, which appear under the microscope of the three following forms: *a.* very oblique rhombic tables with acute angles of about 22°; *b.* apparently quadratic tables; *c.* flattened thin prisms, acuminated at the ends with faces forming an angle of 127° with each other, and angles of 117° with the prismatic faces. The angle of 127° is frequently replaced by a face. Melts at 106°, and solidifies on cooling to a laminated crystalline mass. Volatile: the vapour is irritating and suffocating. Has a faint taste and a distinctly acid reaction (Arppe). Laurent's acid was an easily fusible body, forming a dull mass after melting. Wirz obtained an acid in fine white granules, melting at 98°.

| | | | Laurent. | Wirz. | Arppe. |
|---|---|---|---|---|---|
| 18 C............ | 108 | 57·45 | 54·91 | 55·9 | 57·51 |
| 16 H ........ | 16 | 8·51 | 8·11 | 8·2 | 8·67 |
| 8 O............ | 64 | 34·04 | 36·98 | 35·9 | 33·82 |
| $C^{18}H^{16}O^8$ .... | 188 | 100·00 | 100·00 | 100·0 | 100·00 |

Laurent proposed the formula $C^{20}H^{18}O^{10}$, but had some doubts as to the purity of his acid.

When the acid is submitted to *distillation* in a retort, a portion only passes over undecomposed, the greater part being converted into a brown humus-like substance, besides which a little oil is formed. — *Burns* with a luminous flame (Arppe).

*Combinations.* Azelaic acid dissolves in 700 parts of *water* at 15°, and easily in hot water, from which it crystallises. When it is heated with a quantity of water insufficient for solution, the undissolved portion melts to an oil (Arppe).

Azelaic acid is bibasic, and forms especially di-acid salts, $C^{18}M^2H^{14}O^8$. It expels carbonic acid from its combinations. The salts of the alkalis and alkaline earths are soluble, the lime-salt least so; those of the heavy metals are insoluble. A moderately dilute aqueous solution of

the salts is not precipitated by chloride of barium; chloride of calcium throws down an abundant precipitate, or deposits crystals in more dilute solutions; sesquichloride of iron forms a brick-red, sulphate of copper a blue-green precipitate. — The salts are decomposed by dilute hydrochloric or nitric acid, with separation of crystalline azelaic acid.— The di-acid *ammonia-salt* cannot be obtained in solid form (Arppe).

*Potash-salt.* — *Di-acid.* — Crystallises from a syrupy solution in delicate, soft needles, $C^{18}K^2H^{14}O^8 + 4aq.$, which effloresce, and at 100° become anhydrous (Arppe).

*Soda-salt.* — The *di-acid* salt, $C^{18}Na^2H^{14}O^8 + 2aq.$, forms large, transparent laminæ, having a glassy lustre; when the acid is incompletely neutralised, granules of a $\frac{2}{3}$-acid salt, $C^{18}Na^2H^{14}O^8, C^{18}NaH^{15}O^8$, are obtained (Arppe).

*Baryta-salt.* — A. *Half and two-thirds.* — A warm aqueous solution of the acid, neutralised with warm baryta-water, deposits granules of a $\frac{2}{3}$-acid salt, $C^{18}Ba^2H^{14}O^8, C^{18}BaH^{15}O^8$, which crystallises from water in transparent crystals, and when washed with hot water, leaves a di-acid salt (Arppe).

B. *Mono-acid.* — Obtained as a heavy powder by boiling the aqueous acid with carbonate of baryta.

*Strontia-salt.* — *Di-acid.* — The salt with 4 atoms of water is a heavy powder, easily soluble in warm water, from which it is not again deposited. By concentrating the solution, thin crystalline crusts, and a light powder are obtained; on spontaneous evaporation, white granules containing 2 atoms of water are deposited (Arppe).

*Magnesia-salt.* — The salt with 6 atoms of water effloresces from the loss of 4 atoms. It resembles the strontia-salt, and dissolves in nearly equal quantity in hot and cold water: a solution evaporated in a vacuum yields a fine crystalline powder; when it is concentrated by heat, crystalline crusts are obtained (Arppe).

*Alumina-salt.* — $C^{18}H^{16}O^8, Al^2O^3$. Obtained by decomposing the ammonia-salt with a solution of alum. — Amorphous powder, insoluble in water and in aqueous azelaic acid (Arppe).

*Manganese-salt.* — *Di-acid.* — Anhydrous, reddish, difficultly soluble, crystalline powder (Arppe).

*Zinc-salt.* — *Di-acid.* — White, insoluble powder which melts and puffs up when heated. Anhydrous. — The *di-acid lead salt*, $C^{18}Pb^2H^{14}O^8$, is a white powder (Arppe).

*Iron-salt.* — Brick-coloured powder containing, after strongly drying, 27·19 p. c. sesquioxide of iron. Probably $C^{18}H^{16}O^8, Fe^2O^3, 3HO$ (calc. = 27·15 p.c. $Fe^2O^3$) (Arppe).

*Nickel-salt.* — A solution of hydrated oxide of nickel in the acid is evaporated, and the excess of acid is removed from the residue by means of alcohol. The salt remains as an apple-green crystalline powder (Arppe).

*Copper-salt.* — *Di-acid.* — Anhydrous; blue-green. Insoluble in water (Arppe).

*Silver-salt.* Precipitated from the ammonia-salt by nitrate of silver as a fine white powder, which, after washing and drying, does not blacken. Crystallises from a solution in warm dilute nitric acid in small granules (Arppe).

|  |  |  |  |  | Arppe. mean. |
|---|---|---|---|---|---|
| 18 C | 108 | ........ | 26·86 | ........ | 27·31 |
| 14 H | 14 | ........ | 3·48 | ........ | 3·51 |
| 8 O | 64 | ........ | 15·93 | ........ | 15·52 |
| 2 Ag | 216 | ........ | 53·73 | ........ | 53·66 |
| $C^{18}Ag^2H^{14}O^8$ | 402 | ........ | 100·00 | ........ | 100·00 |

Azelaic acid dissolves easily in *ether*, and more easily in *alcohol* (Arppe).

## Conjugated Compounds of the Primary Nucleus $C^{36}H^{34}$.

## Oleate of Methyl.

$$C^{38}H^{36}O^4 = C^2H^3O,C^{36}H^{33}O^3.$$
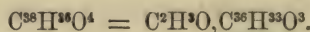
Obtained in the same way as oleate of ethyl and resembles that compound. Sp. gr. 0·879 at 18°. With mercurous nitrate it forms claïdate of methyl (Laurent, *Ann. Chim. Phys.* 65, 299).

## Elaïdate of Methyl.

$$C^{38}H^{36}O^4 = C^2H^3O,C^{36}H^{33}O^3.$$
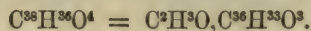
A. LAURENT. *Ann. Chim. Phys.* 65, 294.

*Methyl-elaïdic ether. Elaïdate de Méthylène. Elaïdinformester.*

Prepared from wood-spirit, oil of vitriol, and elaïdic acid or elaïdate of soda, and purified by washing with caustic potash-solution, drying over chloride of calcium, and distilling. — Mercurous nitrate converts oleate of methyl into claïdate of methyl.

Thin colourless oil of sp. gr. 0·872 at 18°, volatile without decomposition. — Burns with a white, almost smokeless flame. It is not acted on by a boiling aqueous solution of potash, but is rapidly decomposed by a boiling alcoholic solution.

|  |  |  |  |  | Laurent. |
|---|---|---|---|---|---|
| 38 C | 228 | ........ | 77·02 | ........ | 75·44 |
| 36 H | 36 | ........ | 12·16 | ........ | 12·40 |
| 4 O | 32 | ........ | 10·82 | ........ | 12·16 |
| $C^2H^3O,C^{36}H^{33}O^3$ | 296 | ........ | 100·00 | ........ | 100·00 |

## Oleate of Ethyl.

$$C^{40}H^{38}O^4 = C^4H^5O,C^{36}H^{33}O^3.$$
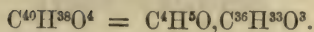
LAURENT. *Ann. Chim. Phys.* 65, 298.
H. MEYER. *Ann. Pharm.* 35, 188.
VARRENTRAPP. *Ann. Pharm.* 35, 206.
BROMEIS. *Ann. Pharm.* 42, 62.
BERTHELOT. *Chimie organique* 2, 83 ; *N. Ann. Chim. Phys.* 41, 245.

*Oleic ether.   Oel-Naphtha.   Ether oléique.   Oëlsäurevinester.*

*Formation and Preparation.* 1. Oleic acid is heated with ⅓ part of oil of vitriol and 2 parts of alcohol for some hours, and the oily layer is washed successively with hot water and hot weak caustic potash, then dried and distilled (Laurent). — 2. Hydrochloric acid gas is passed into a solution of oleic acid in three times its volume of alcohol, when in a few minutes, and before the solution is saturated with the gas, the ether separates. It is removed, freed from admixed oleic acid by shaking with weak alcohol, and from alcohol by shaking with water, and dried (Varrentrapp). — 3. Alcoholic hydrochloric acid decomposes triolein almost completely, forming glycerin and oleate of ethyl, the latter of which retains small quantities of olein (Berthelot).

*Properties.* Thin, colourless oil, of sp. gr. 0·871 at 18° (Laurent). According to Laurent, it distils undecomposed, but according to Varrentrapp and Bromeis, it is decomposed thereby, with formation of alcohol and hydrocarbons, and separation of charcoal. — Nearly inodorous and tasteless (Bromeis).   Neutral.

|  |  |  |  |  |  | Varrentrapp. mean. |  | Bromeis. mean. |
|---|---|---|---|---|---|---|---|---|
| 40 C | ............................ | 240 | ........ | 77·42 | ........ | 76·50 | ........ | 74·17 |
| 38 H | ............................ | 38 | ........ | 12·26 | ........ | 11·94 | ........ | 11·75 |
| 4 O | ............................ | 32 | ........ | 10·32 | ........ | 11·56 | ........ | 14·08 |
| $C^4H^5O,C^{36}H^{33}O^3$ | ... ... | 310 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Concerning the oleic acid of Bromeis see vii, 1485.

*Decompositions.* 1. Oleate of ethyl in contact with *oxygen* absorbs 1 per cent. in 2½ months, and a little more when in contact with brass filings (Berthelot). — 2. *Burns* with white, nearly smokeless flame (Laurent). — *Water* partially decomposes oleate of ethyl in 106 hours at a temperature of 100° ; on the addition of one volume of acetic acid and two to three volumes of water, a considerable amount of decomposition takes place in 106 hours at 100° ; no acetate of ethyl is formed thereby (Berthelot). — 4. Oleate of ethyl is converted, by contact with *mercurous nitrate*, into elaïdate of ethyl, without altering in appearance (Laurent). — 5. Decomposed by alcoholic *potash*, but not by a boiling aqueous solution (Laurent). — 6. When heated to 100° for 200 hours with *hydrochloric acid* and a large excess of *glycerin*, it is converted into olein.   Traces of olein are likewise obtained (Berthelot) by heating with glycerin alone.

Oleate of ethyl is difficultly soluble in *alcohol*, and soluble in all proportions in *ether*.

## Elaïdate of Ethyl.

$$C^{40}H^{38}O^4 = C^4H^5O,C^{36}H^{33}O^3.$$
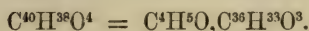
LAURENT.  *Ann. Chim. Phys.* 65, 294.
H. MEYER.  *Ann. Pharm.* 35, 184.

*Ether elaïdique.  Elaïdinnaphtha.  Elaïdinvinester.*

Two parts of elaïdic acid are heated for some hours with 1 part of oil of vitriol and 4 parts of alcohol; or hydrochloric acid gas is passed into an alcoholic solution of elaïdic acid till the elaïdate of ethyl separates.   Purification is effected by washing with water and dilute caustic potash (Laurent), or by shaking with water and alcohol, and then again with water to remove the alcohol taken up (Meyer). — Oleate of ethyl is converted into elaïdate by mercurous nitrate (Laurent).

Thin, colourless oil, inodorous in the cold, but having a faint smell when heated.  Sp. gr. 0·868 at 18° (Laurent).  Boils at a little above 370° according to Laurent; but according to Meyer it is decomposed by distillation.

|  |  |  |  |  | Laurent. distilled. |  | Meyer. *in vacuo.* |
|---|---|---|---|---|---|---|---|
| 40 C | ............................ | 240 | ........ | 77·42 | ........ | 76·02 | ........ | 77·50 |
| 38 H | ............................ | 38 | ........ | 12·25 | ........ | 12·33 | ........ | 12·12 |
| 4 O | ............................ | 32 | ........ | 10·33 | ........ | 11·65 | ........ | 10 38 |
| $C^4H^5O,C^{36}H^{33}O^3$ | ............ | 310 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

*Burns* in the manner of a fatty oil, with white, nearly smokeless flame. — It is not acted on by aqueous *potash*, even when heated therewith, but is rapidly and completely decomposed by boiling alcoholic potash (Laurent).

Insoluble in *water*. — Soluble in *oil of vitriol* (Laurent). — Dissolves easily in absolute *alcohol* (Meyer), in about 8 parts of ordinary alcohol, and in all proportions in *ether* (Laurent).


## Monolein.

$$C^{42}H^{40}O^8 = C^6H^7O^5,C^{36}H^{33}O^3.$$
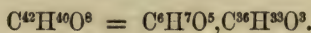
BERTHELOT.  *Chim. organ.* 2, 79 ; *N. Ann. Chim. Phys.* 41, 243.

A mixture of oleic acid and excess of glycerin is heated to 100° for 118 hours, or better to 200° for 18 hours, in a sealed tube which has been previously filled with carbonic acid.  The upper layer, which separates on cooling, contains the olein formed in the reaction, together with excess of oleic acid; it is mixed first with a little water, then with ether and slaked lime, and shaken.  After some minutes more ether and animal charcoal are added, and the whole is again shaken. The ethereal layer which forms on standing contains the olein with a little oleate of lime.  The residue is again treated several times with

ether, and the united extracts are then concentrated in a vacuum, filtered from the oleate of lime which is precipitated, and further evaporated in a stream of dry carbonic acid. The last traces of ether are removed by a gentle heat.

Neutral, yellowish oil, of sp. gr. 0·947 at 21°. Inodorous and nearly tasteless. Solidifies slowly, between 15° and 20°, to a white mass interspersed with crystalline granules. When cooled rapidly to 0°, it becomes solid, and afterwards melts below 10°; but again congeals if kept long at that temperature. Distils undecomposed in a vacuum.

| | | | | | Berthelot. mean. |
|---|---|---|---|---|---|
| 42 C | .................. | 252 | ........ | 70·8 | ........ 71·4 |
| 49 H | .................. | 40 | ........ | 11·3 | ........ 11·5 |
| 8 O | .................. | 64 | ........ | 17·9 | ........ 17·1 |
| $C^6H^7O^5,C^{36}H^{33}O^{33}$ | ........ | 356 | ........ | 100·0 | ........ 100·0 |

Monolein becomes acid in the course of a few weeks when exposed to the air. — Decomposes on heating, with disagreeable smell, burns, and leaves a residue of charcoal. — It is very slowly saponified by moist oxide of lead at 100°, and is not decomposed in 107 hours by alcoholic acetic acid at 100°.

## Diolein.

$$C^{78}H^{74}O^{12} = C^6H^8O^6,2C^{36}H^{33}O^3.$$
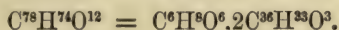
BERTHELOT. *Chim. organ.* 2, 81; *N. Ann. Chim. Phys.* 41, 250.

Monolein is heated to 280° for some hours with 5 or 6 times its weight of oleic acid, or triolein is heated to 200° with glycerin for 22 hours.

Neutral oil of sp. gr. 0·921 at 21°. Begins to crystallise at 10° to 15°.

| | | | | | Berthelot. mean. |
|---|---|---|---|---|---|
| 78 C | .................. | 468 | ........ | 73·35 | ........ 73·5 |
| 74 H | .................. | 74 | ........ | 11·59 | ........ 11·8 |
| 12 O | .................. | 96 | ........ | 15·06 | ........ 14·7 |
| $C^6H^8O^6,2C^{36}H^{33}O^3$ | ........ | 638 | ........ | 100·00 | ........ 100·00 |

## Triolein.

$$C^{114}H^{104}O^{12} = C^6H^5O^3,3C^{36}H^{33}O^3.$$
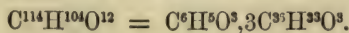
BERTHELOT. *Chim. organ.* 2, 81; *N. Ann. Chim. Phys.* 41, 251.

*Relating to Oil-fat:—*

BRANDIS. *Comment. de ol. unguin. nat.* Gött. 1785.
DEHNE. *Crell. chem. J.* 3, 32.
SCHEELE. *Opusc.* 2, 175.
CHEVREUL. *Recherches,* 185 and 244,

BRACONNOT.    *Ann. Chim.* 93, 225.
SAUSSURE.    *Ann Chim. Phys.* 13, 338; *Schw.* 28, 389; *N. Tr.* 5, 2, 112.
URE.    *Kastn. Arch.* 1, 385; *Schw.* 39, 335; *Repert.* 16, 349.
LIEBIG & PELOUZE.    *Ann. Pharm.* 19, 268.

In an impure state it forms *Huile grasse non siccative*, Braconnot's *Huile absolue*, Chevreul's *elaïn*, afterwards *olein*, as well the *Oelfett* of the third edition of this work. When freed from foreign substances, this body is, according to Berthelot, identical with triolein.

*Source.* Triolein forms the principal constituent of the greasy fat oils, and occurs in smaller quantity in the solid fat. See below.

*Preparation.* A. *From Oleic acid and Glycerin.* Glycerin is heated to 200°, in a sealed tube, with an equal quantity of oleic acid, and the fatty layer which forms is mixed with 15 or 20 times its weight of oleic acid and again heated to 240° for four hours. The triolein, extracted with the help of lime, ether, and animal charcoal (somewhat in the manner described at xvi, 359), is precipitated from its ethereal solution by the addition of 8 or 10 volumes of alcohol, collected on a filter, and dried in a vacuum (Berthelot).

B. *From Fatty oils.* 1. A fatty vegetable oil is cooled to − 5°, when the stearin solidifies and the oil is expressed ; it deposits a little more stearin at −10° (Braconnot). — 2. Lard or tallow is dissolved in boiling absolute alcohol and cooled, whereupon the whole of the olein and only a little of the stearin remain in solution. The solution is distilled with water, which often takes up odorous or colouring substances. The residual oil-fat, after repeatedly washing with water, still deposits a little stearin in the cold (Chevreul). — 3. When olive oil is left in contact with cold caustic soda-solution for 24 hours, the triolein alone remains unsaponified (Kerwyck, *Berth. Chim. organ.* 2, 82).

The product obtained according to 1 and 2 [still containing margarin (Saussure, Pelouze, and Boudet)] is hereinafter distinguished as *oil-fat.*

*Properties.* Neutral oil remaining fluid below − 10° : it volatilises undecomposed in a vacuum and partially at ordinary pressures (Berthelot).

|  |  |  |  |  | Berthelot. mean. |
|---|---|---|---|---|---|
| 114 C | .................... | 684 | ........ | 77·37 | ........ | 77·4 |
| 104 H | .................... | 104 | ........ | 11·76 | ........ | 11·8 |
| 12 O | .................... | 96 | ........ | 10·87 | ........ | 10·8 |
| C$^6$H$^5$O$^3$,3C$^{36}$H$^{33}$O$^3$ | .... | 884 | ........ | 100·00 | ........ | 100·0 |

Oil-fat is colourless, yellow or brown-yellow, and of rather lower specific gravity than the fat of drying oils ; its specific gravity when obtained from olive oil, is 0·915 (Saussure), 0·913 to 0·916 (Chevreul), from goose-fat, 0·929 at 15° (Chevreul). The sp. gr. of natural triolein is 0·914 (Berthelot). For the expansion by heat see Kopp (*Ann. Pharm.* 93, 161). The oil-fat obtained from almond oil does not congeal in the greatest cold ; that from olive oil not at − 10° (Braconnot) but according to Saussure it solidifies at − 4° : the oil-fat from human fat solidifies below − 4°, that from hog's lard at + 7° (Chevreul), at + 9° (Saussure). In the solid

state it is buttery or crystallises in needles. It distils unaltered in a vacuum (Chevreul), and partially so over an open fire (Berthelot). After heating to 216° it is not solid at ordinary temperatures (Berthelot). Inodorous, of mild taste, neutral. Prepared from human fat it contains 77·5 p. c. C., 11·5 H., and 11·0 O.; from hog's lard, 77·9 p. c. C., 11·4 H., and 10·7 O.; from mutton suet, 78·2 p. c. C., 11·1 H., and 10·7 O. (Chevreul). See Saussure (*Ann. Chim. Phys.* 13, 338). Ure (*Schw.* 39, 335). See also vol. vii, p. 237, of this work.

*Decompositions.* See vii, 240. 1. Triolein becomes acid in the *air* (Berthelot). It absorbs in 2½ months, in the dark, 6 per cent. of oxygen, and, if exposed to the light in contact with oxide of lead or brass filings, 8 per cent. (Berthelot). Oil-fat turns rancid in the air, and in thin layers becomes more viscid, but does not dry. — Triolein is not perceptibly altered by *ozone*, but in presence of aqueous caustic alkalis or their carbonates, it absorbs ozone rapidly and continuously, and becomes thick and soapy, evolving an odour of œnanthol. On distilling with water, the product yields a milky distillate, smelling strongly of œnanthol and acrolein, and slightly reducing nitrate of silver; when distilled with phosphoric acid, it yields also formic and propionic acids, whilst palmitic and oleic acids remain in the residue (Gorup-Besanez, *Ann. Pharm.* 125, 213). — 2. Moist *bromine* and *chlorine* convert oil-fat into viscid products which contain 4 atoms of bromine or chlorine to 76 atoms of carbon. — Iodine does not act upon it (Lefort, *Compt. rend.* 37, 29). — 3. Oil-fat is more easily saponified by *alkalis* than tallow or the fat of drying oils (see xvi, 313). When heated with oxide of lead and water, it forms a firmer plaster than drying oil with separation of glycerin. — The decomposition (of triolein and oil-fat) into oleic acid and glycerin is effected (1) by water at 220°, part of the fat, however, remaining unchanged after six hours; (2) by moist oxide of lead at 100°, slowly and with difficulty; (3) incompletely by fuming hydrochloric acid when heated therewith to 100° for 96 hours. Alcoholic hydrochloric acid decomposes triolein almost completely into glycerin and oleate of ethyl; alcoholic acetic acid does not act upon it at 100° (Berthelot). — 4. With *mercurous nitrate* (Poutet), or *nitrous acid* (Boudet), oil-fat solidifies to elaïdin. For the decomposition with oil of vitriol see below.

Triolein dissolves very slightly in *alcohol*, but abundantly in *ether* (Berthelot).

### *Appendix to Triolein.*

# I. Decomposition of Olive Oil by Oil of Vitriol.

FRÉMY. *Ann. Chim. Phys.* 65, 121; *Ann. Pharm.* 19, 296; 20, 50.

When two parts of olive oil are gradually mixed with one part of *oil of vitriol*, so that no heating takes place, the slightly coloured mixture becomes thick and viscous after some minutes without evolving sulphurous acid. When allowed to stand for 24 hours, the products first formed undergo further change, the mixture then containing margarosulphuric, oleosulphuric, and glycerosulphuric acids. On diluting with water, an oily mixture of margarosulphuric and oleosulphuric acids rises to the surface, whilst sulphuric and glycerosulphuric acids remain in solution.

The oily mixture of acids, which cannot be separated into its constituents, dissolves in alcohol and in pure water, but not in water contain-

ing sulphuric acid. Its aqueous solution tastes oily, and afterwards bitter. With the alkalis and ammonia it forms salts soluble in water and alcohol, and with the other bases, salts insoluble in these liquids. Its aqueous solution deposits, at ordinary temperatures, a mixture of metamargaric and metoleic acids, after the removal of which the filtrate, heated to 100°, throws down hydromargaritic and hydroleic acids. Lastly, by heating a fresh aqueous solution of the mixture, hydromargaric acid, formed by the union of the metamargaric and hydromargaritic acids, may be obtained.

a. *Oleosulphuric acid.* On mixing oleic (metoleic or hydroleic) acid with oil of vitriol, a compound is formed which is soluble in water but insoluble in dilute sulphuric acid. Its aqueous solution decomposes slowly in the cold and immediately on boiling, the oleic acid employed being set free. These conjugated sulphuric acids form soluble salts with the alkalis, and insoluble salts with the other bases. The baryta-compound of metoleosulphuric acid contains 2 at. metoleic to 1 at. sulphuric acid.

b. *Margarosulphuric acid.* Margaric acid is precipitated from its solution in oil of vitriol by water unaltered, but when dissolved in oil of vitriol, together with oleic acid, it forms a compound soluble in water.

c. *Metamargaric acid.* From the mixture of metamargaric and met-oleic acids formed by cold water (see above) the greater part of the met-oleic acid may be separated by pressure. The solid residue, treated with warm alcohol of 36°, gives up principally metamargaric acid, a small quantity only of the metoleic acid dissolving. The metamargaric acid is allowed to crystallise from the solution, and is purified by re-crystallisation. It is also obtained by the dry distillation of hydro-margaric acid. — Nodules, or less frequently, shining laminæ, solidifying at 50° to a nearly transparent mass of soft needles. Contains, on an average, 74·07 p. c. C., 12·62 H., and 13·21 O.; when obtained from hydromargaric acid 75·00 p. c. C., 12·53 H.; the lead-salt contains 59·09 p. c. C., 9·94 H., and 23·81 PbO; the silver-salt 55·34 p. c. C., 9·54 H., and 28·53 AgO. The remaining salts behave like those of palmitic acid : metamargaric acid also forms acid salts. According to Frémy, metamargaric acid is represented by the formula $C^{35}H^{35}O^{4·5}$, and loses $1\frac{1}{2}$ at. of water on combining with oxide of lead or other bases. See Gerhardt (*Traité*, 2, 837).

d. *Metoleic acid.* The metoleic acid obtained as above (c) is freed from metamargaric acid by repeated boiling with alcohol and at last by cooling. — Yellowish oil containing 74·77 p. c. C. and 11·90 H. By distilla-tion it is decomposed, in the same manner as hydroleic acid, into car-bonic acid which is evolved during the whole of the process, a little water, followed by a mixture of caproene or oleene (xi, 411) pelargonene or elaene (xiii, 367), and a small quantity of empyreumatic oil. It is insoluble in water, but slightly soluble in alcohol, and easily in ether : it forms easily alterable and generally acid salts, of which those of the alkalis only are soluble in water. The silver-salt contains 60·10 p. c. C., 2·7 H. and 24·73 AgO. Frémy's formula for the acid is $C^{35}H^{32}O^{4·5}$, and for the silver-salt $C^{35}H^{31}AgO^{4·5} + \frac{1}{2}$ aq.

e. *Hydromargaritic acid.* This acid is thrown down, together with

hydroleic acid, when the cold aqueous solution from which the whole of the metamargaric and metoleic acids have been deposited on standing is heated to the boiling-point. The solidified mixture is repeatedly triturated with alcohol of 36°, which dissolves the hydroleic and leaves the sparingly soluble hydromargaritic acid undissolved : the latter is then crystallised from hot alcohol. It crystallises in hard, rhombic prisms which melt at 68°, and are insoluble in water, difficultly soluble in alcohol, but easily in ether. When submitted to dry distillation, it is resolved into water and metamargaric acid. The difficultly soluble salts exhibit the characters of the metaoleates. The acid contains 71·0 p.c. C., and 12·26 H.; the silver-salt 52·66 p.c. C., 8·84 H., and 27·59 AgO: from these numbers Frémy deduces the formula $C^{35}H^{36·5}O^6$ and $C^{35}H^{35·5}AgO^6$. Gerhardt (*Traité*, 2, 837) considers the formula $C^{26}H^{38}O^6$ probable.

f. *Hydroleic acid.* The alcoholic solution obtained in the preparation of hydromargaritic acid is precipitated with water and the acid is cooled to a few degrees below 0° for some time in order to crystallise out the remainder of the hydromargaritic acid. — Slightly coloured oil, easily soluble in alcohol and ether. It is decomposed by dry distillation in the same way as metoleic acid. Contains 73·14 p. c. C. and 11·86 H.; in the syrupy lead-salt, 66·20 p. c. C., 10·57 H., and 11·02 PbO ; in the silver-salt, 59·52 p. c. C., 10·00 H., and 20·09 AgO. Frémy gives for the acid the formula $C^{35}H^{32·5}O^6$, and supposes that the salts retain half an atom of water. On heating the acid with oxide of lead, 1 atom of water is eliminated.

g. *Hydromargaric acid.* When metamargaritic and hydromargaritic acids are mixed in equivalent proportions, or when margaro-sulphuric acid is decomposed by boiling water, and the acid which separates is crystallised from alcohol, hydromargaric acid is obtained in nodules or occasionally small, slightly lustrous needles, melting at 60° and afterwards solidifying to an opaque mass. The acid dissolves in alcohol much more easily than either of those employed in its formation. It contains, on an average, 72·74 p.c. C. and 12·52 H. (Frémy's formula $C^{35}H^{35·5}O^5$) ; in the lead-salt, 56·90 p.c. C., 9·85 H., and 23·45 PbO ; in the silver-salt, 60·76 p. c. C., 10·51 H., and 18·03 AgO. In both these salts, according to Frémy, 1 atom of base takes the place of $\frac{1}{2}$ atom of water ; by heating with excess of oxide of lead, a $\frac{2}{3}$-acid salt is obtained, in which $1\frac{1}{2}$ at. PbO replace 1 at. water. The acid forms a neutral and an acid potash-salt, the latter of which is decomposed by a large quantity of weak alcohol, with separation of free acid.

# II. Fatty Oils occurring in Nature.

Under this head are included the more fully investigated fatty oils which appear to contain ordinary oleic acid. The following memoirs may also be referred to.

On the behaviour of the fatty oils with *oxygen* (Saussure, *Ann. Chim. Phys.* 49, 225 ; *Pogg.* 25, 364) ; with *phosphorus* (Nieper, *Jahrb. pr. Pharm.* 7, 300) ; with *sulphur* (Radig, *N. Br. Arch.* 2, 19) ; with *phosphorus, sulphur, arsenic,* and *chlorine* (Reinsch, *J. pr. Chem.* 13, 136 ; 14, 259) ; with *chloride of sulphur* (Roussin, *Compt. rend.* 47, 877). On the solubility of *arsenious* and *arsenic acids* in fatty oils (Grundner, *Repert.* 61, 289 ; Heimpel, *Repert.* 62, 1 and 19 ; Blondlot, *Compt. rend.*

50, 165). On solubility in *alcohol, ether*, and *acetate of ethyl* (Planche, *Bull. Pharm.* 1, 298; Boullay, *Bull. Pharm.* 2, 260). — On the *saponification* of oils by anhydrous *oxides* (Pelouze, *N. Ann. Chim. Phys.* 47, 371); by *chloride of zinc* (L. Kraft & du Mottay, *Compt. rend.* 48, 410, *Rép. Chim. pure* 1, 269); by *soaps* (Pelouze, *Compt. rend.* 41, 973). On the decomposition of oils by vegetable matters occurring in the seeds (Pelouze, *N. Ann. Chim. Phys.* 45, 319). Concerning the distinction between the several fatty oils and the detection of their adulterations, see Lipowitz (*N. Br. Arch.* 20, 215; 24, 107); Seyfried (*J. pr. Pharm.* 3, 216); Buchner (*Repert.* 69, 264), Heidenreich (*Repert.* 84, 392), Laurot (*N. J. Pharm.* 2, 397), Soubeiran & Blondeau (*J. Pharm.* 27, 65), Fauré (*Dingl.* 77, 350), Gobley (*Dingl.* 91, 384), E. Marchand (*N. J. Pharm.* 24, 267), Maumené, Calvert, Fehling, and Van Kerckhoff (*loc. cit.*), Cailletet (*Rép. Chim. appliquée* 2, 86 and 293), and particularly Chateau (*Mulh. Soc. Bull.* 31, 405, 441, 479, 567; — 32, 211, 261, 317, and 353).

1. *Olive oil.* *Baumöl.* — Obtained from the pulp of the fruit of *Olea europea* (Handbuch, viii, [1], 47). — Concerning the formation of the oil in the olives, see de Luca (*Compt. rend.* 53, 380; 55, 470, and 506). Colourless, or greenish-yellow. Sp. gr. 0·913 (Muschenbroek); 0·9153 (Brisson); 0·915 at 10·5°, 0·9178 at 15°, 0·91635 at 17·5°, the sp. gr. of water at 17·5° being unity (Pohl); 0·9192 at 12°, 0·9109 at 25°, 0·8932 at 50°, 0·8625 at 94°, the sp. gr. of water at 15° being 1 (Saussure). The cold-pressed oil contains 77·36 p. c. C., 11·45 H., and 11·29 O. (Lefort).

Olive oil is resolved by saponification into glycerin and fatty acids. According to the older statements of Chevreul, and of Pelouze & Boudet, these acids are margaric and oleic; according to Collett (*J. pr. Chem.* 64, 108) palmitic and oleic; according to Heintz and Kreig (*J. pr. Chem.* 70, 367), oleic, palmitic, butic, and perhaps also stearic. See further Heintz and Hetzer (*J. pr. Chem.* 64, 111). — Olive oil contains cholesterin (Benecke, *Studien*, p. 108).

Olive oil congeals above 0°, frequently even at 10°, from the crystallisation of small granules. It may be separated, by cooling and pressing, into a fluid and a solid portion. At a temperature of — 6° the solid portion amounts to 28 p. c. (Braconnot) at + 6° to 8° to 33 p. c. (Gusserow). It forms the *stearin of olive oil* or the *oleomargarin* of Pelouze and Boudet, and, according to these chemists, is to be regarded as a definite compound of olein and margarin. — The portion of olive oil which remains fluid on cooling forms the oil-fat of the older chemists, but after more complete separation of the solid portion it is identical with triolein (p. 86).

The stearin of olive oil melts at 20° (Pelouze and Boudet); that obtained by expression at — 2° to 3°, still containing a little oil at 22° (Saussure), 28° (Lecanu). According to Berthelot (*N. Ann. Chim. Phys.* 41, 242), the melting-point never rises above 28°. It dissolves easily in ether, and yields by saponification a mixture of acids which melts at 45° (59° Lecanu), and contains about an equal number of atoms of oleic and margaric acids (Berthelot), the melting-point of which cannot be raised by re-crystallisation (Lecann). Gusserow (*Kastn. Arch.* 19, 77) obtained, by expressing olive oil at a temperature between 6° and 8°, ⅓rd of stearin, melting at 20° to 25°, which, on standing for a long time at a temperature of 15° or 16°, separated into

a fluid and a solid portion. The latter, when saponified with oxide of lead, yielded acids melting at 64°, and forming lead-salts, from 100 parts of which ether took up 63 parts of oleate of lead.

Olive oil boils at 315° (Saussure). It becomes paler at 120°; nearly colourless at 200°; smells and tastes rancid after cooling; boils at a temperature rising from 328° to 394° with decomposition, and after boiling for some time appears dark golden-yellow and syrupy, and deposits sebacic acid (Pohl, *Wien. Acad. Ber.* 12, 80; *J. pr. Chem.* 63, 400). — Olive oil, submitted to dry distillation, behaves like poppy oil (Bussy and Lecanu). By slow boiling an unctuous distillate is obtained, from which, by pressing and crystallising from hot alcohol, Varrentrapp's margaric acid, melting at 55° to 56°, may be obtained. It is still, however, contaminated with margarin (xvi, 351), which may be removed from the potash-salt by ether, after which the acid melts at 60°, and contains 74·82 p. c. C. and 12·42 H. (Varrentrapp, *Ann. Pharm.* 35, 65). Probably palmitic acid (xvi, 351) (? Kr.). — Olive oil yields, besides water and gas, a distillate, which is the more limpid the more quickly the distillation is conducted, and which does not solidify when the oil is made to boil from the commencement. By distilling at a temperature at which boiling does not take place, and heating more strongly when nothing more passes over, it yields at first an unctuous, and afterwards a fluid, acid, yellow distillate. The former distillate is thinner and yellowish at the beginning, then more solid and white, and at last, when the distillation below the boiling point is nearly at an end, again yellowish. The whole of this distillate is of the consistence of lard, solidifies at 20°, and has a disagreeable smell and an acid reaction. It gives up to water a non-acid, odorous principle, sebacic acid, an acid resembling butyric acid, and a brown substance, whilst oleic and margaric (or stearic) acids and a non-acid fatty oil remain behind (Dupuy, *Ann. Chim. Phys.* 29, 319; 32, 53). — Cotton-wool soaked in olive oil takes up 2·8 p. c. of oxygen when exposed to the *air* for two months (Vogel, *Dingl.* 156, 147). — — The oil mixed with platinum-black in a stream of oxygen, and heated to 80° or 90°, yields carbonic acid (Reiset & Millon). — With ¼th of its weight of *flowers of sulphur* it forms, when moderately heated, a dark-brown, tenacious ointment, which dissolves in all proportions in ether, and is precipitated by alcohol. This body forms, with ammonia-water, a yellow liniment, which is not blackened by salts of lead; with caustic potash-solution it becomes thick, and on boiling swells up, and is converted into a jelly (Brandes, *Br. Arch.* 39, 77). — Treated with moist *bromine*, according to xvi, 316, olive oil forms a pale-yellow viscid product of sp. gr. 1·276 at 9·5°, containing 36·42 p. c. of bromine, and forming Lefort's *brominated olive oil*, for which he gave the formula $C^{36}Br^2H^{30}O^4$. See also Knop (*Pharm. Centr.* 1854, 321, 403, 498). — *Chlorinated olive oil*, $C^{36}Cl^2H^{30}O^4$, obtained by the action of moist *chlorine*, is colourless, of sp. gr. 1·078, and contains 20·74 p. c. of chlorine (Lefort, *N. J. Pharm.* 23, 345). Concerning the behaviour of olive oil with chloride of lime, see Lipowitz (*N. Br. Arch.* 20, 215). — *Chlorochromic acid* produces a violent reaction, the oil becoming heated and frothing up (Thomson, *Pogg.* 31, 607). — *Chloride of sulphur* dropped into olive oil causes it to solidify to a yellow, translucent, caoutchouc-like jelly, which is not altered by water, alcohol, or ether (Rochleder, *Dingl.* 111, 159). — Olive oil is coloured light-green by agitation with ⅕th its

volume of syrupy *phosphoric acid,* and also, in 15 minutes, when shaken with an equal volume of *sulphuric acid* of sp. gr. 1·475 to 1·635, or in five minutes with *nitric acid* of sp. gr. 1·18 to 1·33. Shaken with ⅓th its volume of nitrosulphuric acid it is coloured bright orange-yellow in two minutes (Calvert, *J. pr. Chem.* 61, 354). — When 10 cub. cent. of oil of vitriol are cautiously poured into 50 grammes of olive oil, the temperature rises to 42° in two minutes without liberation of sulphurous acid (Maumené, *Compt. rend.* 35, 572). See Fehling (*Dingl.* 129, 53). — Olive oil solidifies with *hyponitric acid* and *mercurous nitrate,* elaïdin (p. 98) being formed. — With alcoholic *ammonia* it forms a large quantity of an amide, solidifying at 97° (Carlet). — It is coloured yellow when heated to boiling with ⅓th its volume of solution of caustic *potash* of sp. gr. 1·34 (Calvert). Concerning the products of saponification see above. It is also saponified by heating 40 parts of the oil with 100 parts of *lime-soap* and an equal quantity of water to 155°—165°, whereas water alone does not act upon it at this temperature (Pelouze, *Compt. rend.* 41, 973 ; *J. pr. Chem.* 68, 141). — *Sodium* and *potassium* become oxidised in olive oil, and form soaps (Gay-Lussac & Thenard). — Olive oil, heated with *oxide of manganese,* forms a manganese-soap, with evolution of carbonic acid (Scheele). See vii, 243.

*Phosphorus* dissolves in 36 parts of olive oil at 15°, and in 25 parts at 100° (Buchholz). — A solution of *selenium* in olive oil, in a fluid state, is orange-yellow and clear by transmitted, pale-red and cloudy by reflected, light ; at ordinary temperatures it is unctuous, and loses its colour on becoming solid, but regains it when melted (Berzelius). — Olive oil dissolves very slightly in *wood-spirit* and *alcohol,* and in 1½ parts (Lecanu), 2·7 parts (Brande) of cold *ether.* From a mixture of 3 parts of olive oil and 2 parts of ether, alcohol does not take up any ether (Planche). Olive oil dissolves in 5 parts of *acetic ether* (Planche).

2. *Almond oil.* — From the kernels of *Amygdalus communis* (*Handbuch,* viii, [1] 14). Sweet and bitter almonds yield oils of the same nature. — Colourless or yellowish ; sp. gr. 0·911 (Brandis), 0·917 (Brisson), 0·918 at 15° (Schübler), 0·92 at 12°, that of water at 15° being in unity (Saussure). Expands on heating in precisely the same way as olive oil (*J. Chim. méd.* 20, 65). Almond oil is thicker than poppy oil, thinner than olive oil ; it becomes thick at − 10°, cloudy at − 16°, and solidifies at − 21° to a white butter (Schübler). It solidifies at + 6° (Fourcroy), at − 10 to 11° (Braconnot), not at − 11°, but slowly at − 18° (Brandis). Braconnot (*Ann. Chim.* 93, 241) separated it, by pressing at − 10°, into 76 parts of an oil which did not solidify in the most intense cold, and 24 parts of stearin melting at 6°. According to Gusserow (*Kashtn. Arch.* 19, 79) it solidifies at − 10 to 12° to a homogeneous mass, which remains solid at − 5 to 6°, but gradually liquefies at − 2 to 3°, and does not admit of separation into portions of different melting-points. From the lead-salts of the fatty acids of almond oil, ether takes up about 77 p. c. of oleate of lead (Gusserow). Ether dissolves the lead-plaster formed from almond oil almost completely, leaving only traces of the lead-salts of solid fatty acids (Kr.). — The oil expressed from bitter almonds contains, on an average, 70·53 p. c. C., 10·61 H., and 18·66 O. ; that from sweet almonds 70·48 p. c. C., 10·64 H., and 18·88 O. (Lefort).

Almond oil turns rancid in the *air.* — It does not yield margaric acid by *distillation* (Anderson). See xvi, 351. — *Phosphorus* dissolves in

36 parts of almond oil at 15°, and in 31 parts at 100° (Buchholz). Almond oil, heated with phosphorus, behaves in the same way as poppy oil (Jonas). — *Sulphur*, warmed in almond oil, melts to an oily layer beneath the surface, and when further heated, dissolves to a dark red, thick, glutinous liquid which swells up at the temperature of decomposition of the oil, with abundant and continuous evolution of hydrosulphuric acid, and yields a distillate of dark-brown, repulsive-smelling oil, from which margaric acid is deposited on cooling, the portion remaining fluid containing odmyl (x, 97). In this reaction neither acrolein nor sebacic acid is produced (Anderson, *Ann. Pharm.* 63, 370). See also xvi, 351. On boiling 3 parts of *iodine* with 1 part of almond oil and 6 parts of water, most of the iodine distils unchanged, the oil becoming heavy, brown, and viscid (Reinsch, *J. pr. Chem.* 14, 263). —*Bromine* and *chlorine* form with the oil of bitter and sweet almonds products of similar composition ; they are colourless, of the consistence of castor oil, and contain 17·55 p. c. chlorine and 32·56 p. c. bromine. Sp. gr. of the bromine-compound, for which Lefort proposed the formula $C^{20}BrH^{17}O^4$, $= 1·252$ at 19·2°, that of the chlorine-compound, $C^{23}ClH^{17}O^4$ $= 1·057$ at 18·5° (Lefort, *N. J. Pharm.* 23, 282). Concerning the behaviour of almond oil with bromine, see also Knop (*Pharm. Centr.* 1854, 321, 403 and 498) ; with chloride of lime : Lipowitz (*N. Br. Arch.* 20, 215). — Almond-oil is coloured yellow-brown by *oil of vitriol.* When 15 grammes of the oil are mixed with 5 grammes of oil of vitriol, the temperature of the mixture rises to 40·3 (Fehling). *Mercurous nitrate* converts almond oil into a mass which is softer than that formed with olive oil (Davidson, *Ed. N. Phil. J.* 28, 250).

The oil expressed from bitter almonds is oxidised by *nitric acid*, with the same phenomena which occur in the oxidation of castor oil, yielding œnanthylic acid and a non-volatile fatty oil, together with oxalic, succinic, suberic, and azelaic acids (Arppe, *Ann. Pharm.* 120, 292). — Almond oil takes fire with *chlorate of potash* and oil of vitriol (A. Vogel, *Ann. Pharm.* 74, 115). It forms with alcoholic *ammonia* an amide melting at 92° (Carlet, *Par. Soc. Bull.* 1, 73). — When heated with *chloride of mercury* it becomes black, and evolves acid vapours (E. Davy). — Almond oil yields a very hard soap.

Almond oil dissolves in about 25 parts of cold, and 6 parts of hot, *alcohol*, and mixes with *ether* and *chloride of ethyl* (Pfaff). According to Brande, it dissolves very slightly in alcohol of sp. gr. 0·82, and in 3·2 parts of ether, and according to Planche, in 4 parts of *acetate of ethyl.*

3. *Fatty Ant-oil.* — Obtained by expressing the residue which remains in the distillation of ants with water. Saffron-yellow ; tastes mild at first, afterwards irritating (Göbel). Reddish-brown, transparent ; floats on water and solidifies at a moderately low temperature. Forms soap and plaster (Margraf).

4. The almonds of *Anacardium orientale* contain a little sweet oil. The pericarp contains ⅓rd of a blistering oil of sp. gr. 0·991, easily soluble in ether, and turning black in the air (Lepine, *N. J. Pharm.* 40, 16).

5. *Oil of the seeds of Argemone mexicana.* — Orange-yellow, mild. Remains fluid at 8° (J. Lepine).

6. *Oil of Aspidium Filix mas.* — On treating the ethereal extract of the root with water containing ammonia, filicic acid is taken up

thereby, whilst the oil remains dissolved in the ether. — Dark grass-green, thicker than olive oil, tastes first mild and afterwards harsh, and smells like the root. Deposits no solid fat even in winter. Saponifies with some difficulty, and yields a green, soft, friable soda-soap. Contains Luck's filixoleic acid (p. 74) (Luck, *Jahrb. pr. Pharm.* 22, 153). See also Winckler (*Mag. Pharm.* 22, 48).

7. *Oil of the almonds of Azadirachta indica.* — Yellow, of sp. gr. 0·921. Tastes bitter; smells like garlic; congeals at $+ 7°$. Yields by saponification 35 p. c. of fatty acids melting at $30°$, and 65 p. c. melting at $44°$ (Lepine).

8. *Oil of Barley-meal.* — Obtained by exhausting the meal first with water, and afterwards with hot alcohol. Greenish-brown, thick oil, which becomes granular in the cold like olive oil, and smells and tastes like fusel oil. Saponifiable. Dissolves slightly in alcohol, and is precipitated from the solution by water (Fourcroy & Vauquelin, *N. Gehl.* 2, 383).

9. *Oil of Beech-nuts.* — From the kernels of *Fagus sylvatica*. Yellow; has a mild and agreeable taste, and a faint odour. Sp. gr. 0·9207 (Lefebvre), 0·9225 at $15°$ (Schübler), 0·923 (Fabbroni). Thickens and becomes turbid at $- 15°$, and solidifies at $- 17.5°$ to a yellowish-white mass (Schübler). Contains, on the average, 75·11 p. c. C., 11·06 H., and 13·83 O. (Lefort). — With moist chlorine it forms Lefort's *chlorinated beech oil* of sp. gr. 1·084 at $10.5°$, of the consistence of castor oil, and containing 22·72 p. c. chlorine; with moist bromine, *brominated beech oil* of sp. gr. 1·353 at $6.5$, containing 40·57 p. c. bromine. Lefort (*N. J. Pharm.* 23, 342) proposes the formulæ $C^{30}H^{28}O^4$ (for beech-nut oil), $C^{30}H^{26}Cl^2O^4$, and $C^{30}H^{26}Br^2O^4$. — The oil yields a soft soap (Pelletier). It forms, with alcoholic ammonia, a very small quantity of an amide melting at $70°$ (Carlet). — Dissolves in $2\frac{1}{2}$ parts of acetate of ethyl at $12.5°$ (Planche).

10. *Oil of the seeds of Butea frondosa.* — Yellow; of sp. gr. 0·917; nearly tasteless. Solidifies at $10°$ (Lepine).

11. *Oil of the seeds of Calophyllum inophyllum.* — Green-yellow; bitter and aromatic; of sp. gr. 0·942. Solidifies at $+ 5°$ (Lepine).

12. *Oil from the nut of Canarium commune.* — Moderately mobile; colourless. Tastes sweetish. Assumes the consistence of honey in the cold, from crystallisation of stearin. Contains 47 parts of stearin to 53 parts of oil-fat. Turns rancid in a year. The fresh oil deposits stearin at a temperature of $15°$, but after keeping for eight months, the stearin is deposited only at $- 2.5°$ (Bizio, *Bibliot. ital.* 1823, No. 91, p. 60).

13. *Oil of the almonds of Cassuvium pomiferum* (the cashew-nut). — Sweet, pale yellow oil of sp. gr. 0·916. The pericarp of the nut contains a thick viscid blistering oil of sp. gr. 1·014, which reddens litmus and turns darker in the air. Dissolves in alcohol and ether with the exception of some white flocks. Dyes linen a permanent yellow-red (Lepine).

14. *Oil of Cotton-seeds.* — Contains palmitin and a large quantity of olein (Slessor, *N. Edin. Phil. Journ.* 9, 11; *Chem. Centr.* 1859, 140. — See also Williams (*Dingl.* 43, 239), who appears to regard it as a drying oil. — Sp. gr. 0·9306 at $15°$ (Lefebvre).

15. *Croton oil.* — From the fruit of *Croton Tiglium* (*Handbuch*, viii [1], 23). — Thick brown oil, having a strong rancid odour. Acts as a violent purgative. When rubbed upon the skin, it produces inflammation, the oil obtained from the press-cake by displacement with alcohol being more active in this respect than the expressed oil. Becomes cloudy on slight cooling, from separation of solid fatty acids. Croton oil dissolves in 23 parts of alcohol of 85 p.c. The neutral, bright-yellow oil which has been freed from admixed resin and free fatty acids by shaking with alcoholic potash, requires 35 parts of alcohol for solution (Schlippe). According to earlier statements it is easily soluble in alcohol. — Croton oil is not solidified by nitrous acid. — On exposure to the air, it forms a thick viscid mass, differing from that formed with poppy oil, and probably resulting only from the liberation of fatty acids, and not from the decomposition of drying oil acids (Schlippe). A mixture of croton oil and alcoholic ammonia deposits crystals of an amide which, after re-crystallisation from alcohol, melts at $100°$, and has the composition of margaramide $C^{34}NH^{35}O^2$ (Rowney, *J. pr. Chem.* 67, 160). Croton oil yields, when saponified, a brown soap and a black mother-liquor, which is decolorised by acids (Schlippe).

Croton oil contains crotonol (xiii, 376), together with a decomposition-product thereof, to which it owes its smell; also stearic, palmitic, myristic, lauric (this acid passes over together with a decomposition-product of croton oil on boiling the seeds with water), angelic (x, 413), and crotonic ($C^8H^6O^4$) acids in the form of glycerides. A mixture of the last two acids appears to form the *jatrophic acid* of Pelletier & Caventou, and the *crotonic acid* of the older chemists. Croton oil contains two other members of the oleic acid ($C^nH^{n-2}O^4$) series, probably $C^{34}H^{32}O^4$ and $C^{20}H^{18}O^4$ (Schlippe, *Ann. Pharm.* 105, 1).

The lime-soap obtained from croton oil dissolves partially in ether with yellow-brown colour. On distilling off the ether, decomposing the residue with carbonate of potash, and precipitating the resulting solution of the potash-soap with chloride of barium, a baryta-soap is obtained, which, after washing and drying, exhibits the following behaviour. It gives up to boiling alcohol a portion which crystallises from the filtrate, melts easily to a clear oil, and contains $22·9$ p.c. baryta ($? C^{34}H^{31}BaO^4 = 22·84$ p.c. BaO). From the portion remaining undissolved after twice boiling with alcohol, ether takes up a baryta-salt containing $32·12$ p.c. baryta ($? C^{20}H^{18}O^4 = 32·2$ p.c. BaO). The baryta-salts obtained by four times repeated boiling with alcohol contain $24·7$, $23·02$, $23·1$ and $29·2$ p.c. baryta. Hence Schlippe supposes croton oil to contain two or more liquid acids belonging to the same series as oleic acid, but differing therefrom.

16. *Oil of the seeds of Daphne Mezereum. Oleum Seminum Coccognidii.* — Extracted from the bruised seeds by boiling alcohol. Greenish-yellow or yellow. Sp. gr. $0·914$, of that obtained from very old seeds $0·921$. Acts as an irritant and vesicant. When the alcohol which has been used for its extraction is cooled to $-12·5°$, the oil floating on the surface being first removed, it deposits fatty granules which do not possess blistering properties after purification (Martius, *N. Br. Arch.* 110, 39).

17. *Oil of Earth-almond.* — From the roots of *Cyperus esculentus*. Sp. gr. $0·918$. Smells like hazel-nuts, and has a slightly camphory, not disagreeable taste. Deposits stearin. Yields a good soap with

soda. Dissolves with difficulty in alcohol, but very easily in ether, and in 30 parts of acetate of ethyl (Lesant, *J. Pharm.* 8, 509).

18. *Oil of Eggs.* — Obtained by expressing hard-boiled and warmed yolks of eggs, or by exhausting them with ether, the two processes, however, yielding different products. — The oil obtained by expression is reddish-yellow, thick, tasteless or of mild taste, and neutral. On long standing it deposits stearin, and at 4° to 6° solidifies to a granular mass, which leaves on the filter more stearin, melting at 56°. The oil freed from stearin is thicker than linseed oil, thinner than olive oil, and congeals at 0° to a non-crystalline mass (Planche, *J. Pharm.* 1, 438). Egg oil contains $\frac{1}{300}$th of cholesterin, which is deposited in laminæ when the oil is kept at a temperature of 12—15° (Lecanu, *J. Pharm.* 15, 1). It contains volatile acid (Redtenbacher). — Dissolves in 22·5 parts of alcohol of 90 p. c. on digesting for 24 hours, with partial separation of stearin. — Egg oil extracted by ether is of a fine yellow colour, not red (Mialhe & Walmé, *J. Pharm.* 16, 128). It is sharp, smells disagreeable, absorbs oxygen, and contains besides egg oil proper, the viscous substance (xvi, 484) which is left behind on filtration, and remains in the press-cake, when the oil is obtained by expression. The expressed oil, as well as that extracted by ether and freed from the viscous matter, congeals at − 6° to a crumbly mass in which many laminæ of cholesterin are discernible. Both oils deposit in the cold a mixture of oil-fat, margarin-fat, cholesterin, and colouring matter; they are free from phosphorus and sulphur, and differ from other oils only in containing cholesterin and colouring matter (Gobley, *N. J. Pharm.* 9, 12; *Compt. rend.* 21, 989). The blackening of silver by eggs is owing to sulphur in the albumin, and not to an oil containing sulphur (Gobley). That portion of the oil extracted by ether which is insoluble in alcohol (and thereby separated from the viscous matter) is a slightly coloured, mild, semi-solid fat, difficult to saponify, yielding by Gusserow's method oleic acid, and in addition stearic acid (contrary to Gobley, who found only margaric), margaric acid, and perhaps also a third acid richer in oxygen (Kodweiss, *Ann. Pharm.* 59, 261). — The oil extracted by ether from ducks' eggs is of a darker golden-yellow colour, and less viscid than that of hens' eggs, and does not possess the peculiar odour of the latter oil (Geissler, *N. Br. Arch.* 11, 168).

19. *Fatty oil of Ergot-of-rye.* — A hot alcoholic solution of the brown fat extracted by ether deposits the greater part in a colourless state on cooling. It forms a thick, somewhat rancid oil of sp. gr. 0·922 at 7·5°. Solidifies partially at 0°, and completely at − 37°. When boiled in a glass tube it is converted into very acid vapours which smell like those of other fatty oils, leaving a very little charcoal. It is not saponified, or only to a slight extent, by boiling with potash. Insoluble in cold, and soluble only in a large quantity of boiling alcohol, but easily soluble in ether (Wiggers, *Schw.* 64, 164). See Wrigt (*Pharm. Centr.* 1840, 524) who obtained a saponifiable fat soluble in alcohol.

20. *Oil of Euphorbia Lathyris* (*Handbuch*, viii [2], 24. — Pale-yellow oil of sp. gr. 0·9201, congealing at − 11·25°. — The oil extracted by alcohol or ether contains a white crystalline body, a brown oil, a resin, and other substances (Soubeiran, *J. Pharm.* 21, 259; *Br. Arch.* 33, 227). The oil extracted by ether (Fleurot) and the expressed oil (Chevallier) deposit white needles on keeping (*J. Chim. méd.* 5, 356).

21. *Hazel-nut Oil.* — From the shelled nuts of *Corylus Avellana.*— Thick, pale-yellow or nearly colourless, inodorous oil having a mild, agreeable taste. Sp. gr. 0·9242 at 15°. Becomes very thick at − 15° to 16°, and congeals at − 19° to a yellow-white mass (Schübler). Contains 77·4 p. c. C., 11·6 H., and 11·0 O. The colourless *chlorinated* oil of sp. gr. 1·081 at 3·5°, contains 20·65 p. c. of chlorine : the yellowish *brominated* oil is of sp. gr. 1·28 at 2·3°, and contains 36·47 p. c. of bromine (Lefort). Lefort's formulæ are $C^{36}H^{32}O^4$, $C^{36}Cl^2H^{30}O^4$, and $C^{36}Br^2H^{30}O^4$. — With alcoholic ammonia it forms oleamide (Carlet). Dissolves in 7 parts of acetate of ethyl at 12·5° (Planche).

22. *Oil of Horse-chestnuts.* — From *Aesculus Hippocastanum.* Golden-yellow; of sp. gr. 0·927; solidifies at 1·25°; smells and tastes like beet. Easily saponifiable. — Vauquelin extracted from the scales of *Aesculus Hippocastanum,* with hot alcohol, an inodorous, green-yellow, rancid oil which yielded a moderately firm soap with soda.

23. *Oil of the fruit of Mesua ferrea.* — Chestnut-brown oil of sp. gr. 0·954, solidifying at 5° (Lepine).

24. *Oil of Morels.* — From *Helvella Mitra.* Thick oil lighter than water, having the smell and taste of morels. Forms a hard soap with soda. Dissolves in alcohol and ether (Schrader). Morels contain also a white, crystalline, pearly, and tolerably hard fat resembling spermaceti. It melts on platinum to a clear oil, burns with a somewhat fatty odour, and leaves charcoal. Dissolves easily in cold alcohol and ether, slowly in olive-oil (Schrader, *Schw.* 33, 593).

25. *Oil of the seeds of Nigella sativa.* — Orange-yellow ; of sp. gr. 0·92 ; congeals at 2°. Smells aromatic and camphory (Lepine).

26. *Fatty oil of the root and seeds of Paris quadrifolia.* — Extracted by ether from the roots and seeds which have been previously exhausted with water and alcohol, and freed from paridin and resin by treatment with cold alcohol of sp. gr. 0·85. — Green-yellow, non-drying oil of sp. gr. 0·935. Dissolves with difficulty in alcohol, but easily in ether. The acid separated from the soap solidifies easily (Walz, *J. pr. Pharm.* 6, 10).

27. *Oil of Parsley.* — From the seeds of parsley. The powdered seeds are exhausted with alcohol and the tincture is decolorised by animal charcoal and ¾ths of the alcohol are distilled off ; the residue is then exhausted with ether or chloroform; the extract is again submitted to distillation, and the last traces of ether or chloroform are allowed to evaporate spontaneously in a basin. The residual liquid is triturated with ⅛th of its weight of litharge, left to stand for 48 hours, and lastly filtered through charcoal. — Colourless oil of sp. gr. 1·078 at 12°, becoming cloudy at − 12° without solidifying. Tastes sharp and biting, smells strongly of parsley seeds, and has a faintly acid reaction. Deflects a ray of polarised light slightly to the left. Free from nitrogen. Febrifuge. — Evolves a few bubbles at 150 to 175°, and becomes coloured at 220°, without losing weight or being essentially altered. Combustible. Assumes a splendid red colour with *oil of vitriol* and solidifies, losing its taste and smell. Parsley oil is converted into a resin by *nitric acid,* but is not altered by *hydrochloric acid. Potassium* evolves gas-bubbles, and dissolves. Parsley oil forms an emulsion

with *alkalis* without undergoing further change; after agitation with ammonia it remains unaltered. — The oil is insoluble in *water*, but easily soluble in *alcohol* of 50 to 60 p. c.; alcoholic neutral acetate of lead produces in the solution a strong cloudiness which disappears on warming and appears again in the cold. — Parsley-oil dissolves in *acetic acid* and in all proportions in *ether* and *chloroform* (Homolle and Joret, *N. J. Pharm.* 28, 212; *Pharm. Viertelj,* 5, 253). It is doubtful whether this body must be considered as belonging to the fatty oils (Kr.).

28. *Oil of Plum-kernels.* From *Prunus domestica.* Yellow-brown oil, of sp. gr. 0·9127 at 15°, thinner than oil of brassica, thicker than hemp oil. Becomes cloudy at − 6° from separation of white flocks, and solidifies at − 8·7° to a yellowish mass. Has an agreeable taste and smell of almonds. Easily turns rancid, and remains greasy when exposed to the air (Schübler).

29. *Oil of the seeds of Pongamia glabra.* — Dark-yellow oil of sp. gr. 0·945, having a poisonous odour and bitter taste. Solidifies at 8° (Lepine).

30. *Sesame oil.* — From the fruit of *Sesamum orientale.* Golden-yellow, somewhat darker than almond oil. Inodorous, and having a slight taste of hemp. Sp. gr. 0·9143 at 11° (Lefort); 0·9235 at 15° (Lefebvre); 0·923 at 15°, 0·921 at 17·5, 0·9183 at 21·3°, water at 17·5° being 1 (Pohl). Contains on an average, 70·44 p. c. C., 10·74 H., and 18·82 O. (Lefort). — Remains clear at 4°, and solidifies at − 5° to a yellow-white, homogeneous mass (Pohl). Becomes rancid on standing in the air. The oil is decolorised by heating to 150—215°, evolving white vapours at the latter temperature, and appearing, after cooling, brighter than at first; it becomes darker and yellowish-brown at 300°, and boils at 335—390° with decomposition (Pohl). — Sesame oil forms with *chlorine* a viscid yellow compound, darker than the oil, of sp. gr. 1·065 at 6°, and containing 17·24 p. c. of chlorine. The *bromine-compound* contains 32·61 p. c. of bromine; its sp. gr. at 18° is 1·251. Lefort proposes the formulæ, $C^{20}H^{18}O^4$, $C^{20}ClH^{17}O^4$, and $C^{20}BrH^{17}O^4$ (Lefort, *N. J. Pharm.* 23, 285). — Sesame oil is not coloured by shaking with ¼th its volume of syrupy phosphoric acid. When shaken with an equal volume of sulphuric acid of sp. gr. 1·475 to 1·53, it appears greenish after 15 minutes; treated in the same way with nitric acid of sp. gr., it is coloured in five minutes orange-yellow, and with an acid of sp. gr. 1·22 or 1·33, red (Calvert, *J. pr. Chem.* 61, 354). Oil of vitriol forms with sesame oil a red-brown jelly, which evolves sulphurous acid when heated; water throws down therefrom a curdy, white and purple precipitate (Pohl, *Wien. Akad. Ber.* 12, 80; *J. pr. Chem.* 63, 400.)

31. *Fatty oil of Silkworms.* — Obtained by extracting with alcohol, and washing the extract with hot water. Brown-green oil, remaining fluid at 0°. Lighter than water. Neutral. Dissolves easily in cold alcohol and ether. Easily saponifiable by caustic potash; less easily by oxide of lead, yielding stearic acid, and a liquid acid, probably oleic (Lassaigne, *J. Chim. méd.* 20. 471).

32. *Spindle-tree oil.* From the seeds of *Euonymus Europæus* (*Handbuch.* viii., [2] 22). According to Schübler, a red-brown oil of repulsive odour and taste; according to Schweizer, bright-yellow, smelling

like rape-oil, and having a bitter, afterwards harsh taste. Sp. gr. 0·938 at 15°, being the heaviest oil after castor-oil (Schübler). Viscid oil, becoming thicker at − 16°, with deposition of stearin, and solidifying at − 20° to a red-brown mass (Schübler). Solidifies at − 12 to 15°, and deposits colouring matter (Schweizer). Non-drying (Riederer). Gives up to warm water a bitter substance, but no free acid. Dissolves with difficulty in alcohol, the solution having an acid reaction. Not precipitated from its ether-alcoholic solution by alcoholic neutral acetate of lead. — The yellow potash-soap is decomposed by acids, oleic and margaric acids being separated, whilst benzoic and acetic acids remain in solution. The benzoic acid is present in the oil in the free state, the acetic acid as glyceride (Schweizer, *J. pr. Chem.* 53, 437; *Ann. Pharm.* 80, 288; *Lieb. Kopp's Jahresb.* 1851, 444). See also Riederer (*Kastn. Arch.* 6, 413; *Ann. Pharm.* 8, 209). His *euonymin* was obtained by evaporating an ether-alcoholic solution of the oil with magnesia, exhausting the residue with alcohol, evaporating and exhausting with ether.

33. *Oil of the seeds of Sterculia fœtida.* — Bright-yellow, of sp. gr. 0·923, not congealing at 3° (Lepine).

34. *Oil of various species of Thea or Camelia.* — Used in China as olive oil. Inodorous, and of straw-yellow colour. Does not solidify at 5·5°, but resembles an emulsion at 4·5°. Sp. gr. 0·927. Contains 25 parts of stearin and 75 of olein. Insoluble in alcohol, and very slightly soluble in ether (Thomson, *J. Chim. méd.* 13, 409; *Dingl.* 66, 240).

35. *Fatty Oil of Truffles.* — The oil extracted by ether is greenish-brown, rancid; tastes sharp and harsh; reddens litmus, and is heavier than water. It deposits stearin on standing, and yields traces of volatile oil when distilled. Saponifiable; soluble in hot alcohol (Riegel, *Jahrb. pr. Pharm.*, 7, 225).

## Elaïdin.

$$C^{114}H^{104}O^{12} = C^6H^5O^3,3C^{36}H^{33}O^3.$$
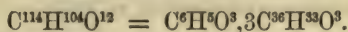
*Literature, History, and Formation* (p. 74).

The product of the action of mercurous nitrate or hyponitric acid on olive oil is dissolved in a small quantity of ether, and the filtered solution is cooled to 0°, whereupon the elaïdin crystallises in nodules. It is freed from the red mother-liquor, by washing with cold ether (Meyer). Boudet boils the impure elaïdin with alcohol, but Meyer did not succeed in decolorising and purifying it by this method.

White mass resembling stearin and melting at 32° (Meyer), 36° (Boudet). Like stearin it has two different melting-points, the first of which is 23·7°, the second 28° (Duffy). See further under Tristearin.

|  |  |  |  |  | Meyer. *mean.* |
|---|---|---|---|---|---|
| 114 C .............................. | 684 | ........ | 77·37 | ........ | 76·96 |
| 104 H ............................... | 104 | ....... | 11·76 | ........ | 12·03 |
| 12 O ................................. | 96 | ........ | 10·87 | ........ | 11·01 |
| $C^6H^5O^3,3C^{36}H^{33}O^3$ ........ | 884 | ........ | 100·00 | ........ | 100·00 |

The elaïdin investigated by Meyer still contained margaric acid, which he was unable to separate by recrystallization : hence the above formula and the view of Gerhardt (*Précis* 1, 179), who regarded elaïdin as isomeric with olein (triolein), are rendered doubtful. Elaïdin may possibly be a compound of glycerin with two different acids, corresponding to the oleomargarin of olive oil (Kr.).

*Decompositions.* Elaïdin submitted to dry *distillation*, emits a strong penetrating odour, evolves gases, and yields a fluid distillate which is buttery on cooling, and contains water, acetic acid, elaïdic acid, and volatile and empyreumatic oil. Towards the end of the distillation sebacic acid is obtained, a small quantity of charcoal remaining behind (Boudet). Meyer, by the dry distillation of elaïdin, obtained acrolein, elaïdic acid, hydrocarbons, and perhaps sebacic acid. — Elaïdin yields by *saponification*, elaïdic acid (Boudet) ; a mixture of elaïdic and margaric acids, melting at 38·5°, which cannot be separated into the pure acids re-crystallisation (Meyer). — *Hyponitric acid* forms with elaïdin a fluid compound containing an acid richer in oxygen and the elements of ammonia (Pelouze and Boudet, *Ann. Pharm.* 29,47).

Elaïdin dissolves in 200 parts of boiling *alcohol* of sp. gr. 0·898, and also to a slight extent in stronger alcohol, and in all proportions in *ether*.

## Mannitic Bioleate.

$$C^{84}H^{76}O^{14} = C^{12}H^{10}O^8,2C^{36}H^{33}O^3.$$
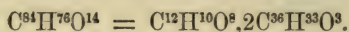
BERTHELOT. *N. Ann. Chim. Phys.* 47, 326 ; *Chim. organ.* 2, 192 ; *Lieb. Kopp. Jahresb.* 1856, 660.

*Mannite oléique. Bioleïnmannitanester* (p. xv, 362).

Obtained in the same manner as the corresponding palmitic compound (xvi, 380). The ether employed in its extractionl ikewise takes up oleate of lime, which is deposited when the ethereal solution is made to boil in a vacuum.

Nearly colourless, neutral, waxy mass, becoming soft and tenacious at a gentle heat, and afterwards melting to a yellowish liquid. On evaporating its solution in a vacuum, it remains as a spongy, distended elastic mass. — When heated with hydrate of lime, it is resolved into mannitan and oleic acid. — Dissolves in ether.

|  |  |  |  |  | Berthelot. |
|---|---|---|---|---|---|
| 84 C ............................... | 504 | ........ | 72·82 | ........ | 72·3 |
| 76 H ............................... | 76 | ........ | 10·98 | ........ | 11·4 |
| 14 O ............................... | 112 | ........ | 16·20 | ........ | 16·3 |
| $C^{12}H^{10}O^8,2C^{36}H^{33}O^3$ ........ | 692 | ........ | 100·00 | ........ | 100·0 |

After deducting 3 p. c. of ash.

*Bromine-nucleus* $C^{36}Br^2H^{32}$.

## Bromoleic Acid.

$$C^{36}Br^2H^{32}O^4 = C^{36}Br^2H^{32},O^4.$$
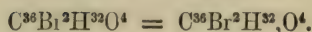
LEFORT. *Compt. rend.* 37, 28; *J. pr. Chem.* 60, 179; *Pharm. Centr.* 1853, 491; in detail *N. J. Pharm.* 24, 113.

Oleic acid treated with bromine and water, according to xvi, 316, is converted into a brown oil of sp. gr. 1·272 at 7·5°, which boils at 200°, and reddens litmus. Contains, on an average, 36·45 p. c. of bromine (calc. = 36·36 p. c. Br).

*Chlorine-nucleus* $C^{36}Cl^2H^{32}$.

## Chloroleic Acid.

$$C^{36}Cl^2H^{32}O^4 = C^{36}Cl^2H^{32},O^4.$$

LEFORT. *N. J. Pharm.* 24, 113.

Obtained from chlorine and oleic acid in presence of water, according to xvi, 316.
Brown oil of sp. gr. 1·082 at 8°, thicker than oleic acid. Reddens litmus. Boils at 190°. Contains on an average 20·61 p. c. of chlorine (calc. = 20·23 p. c. Cl).

*Amidogen-nucleus* $C^{36}AdH^{33}$.

## Oleamide.

$$C^{36}NH^{35}O^2 = C^{36}AdH^{33},O^2.$$
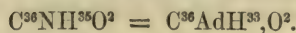
BOULLAY. *N. J. Pharm.* 5, 329; abstr. *J. pr. Chem.* 32, 223; *Compt. rend.* 17, 1346.
ROWNEY. *Trans. Roy. Soc. Edin.* 21, part 2; *Chem. Gaz.* 1855, 361; *J. pr. Chem.* 67, 157; abstr. *Lieb. Kopp's Jahresb.* 1855, 531; Prelim. notice: *Chem. Soc. Qu. J.* 7, 200; *Lieb. Kopp. Jahresb.* 1854, 465.
CARLET. *Par. Soc. Bull.* (1859) 1, 73; abstr. *Lieb. Kopp. Jahresb.* 1859, 366.

The transformation of fats by ammonia was investigated in 1844 by Boullay, who, however, did not prepare the amides in a pure state, and regarded them, even when obtained from different fats, as one and the same product, *margaramide.*

*Formation.* From almond oil (Rowney) or hazel-nut oil (Carlet) and alcoholic ammonia. Seal oil yields, with alcoholic ammonia, an

amide melting at 82° and having the composition of oleamide (Rowney). — The oils are also converted into amides by long standing with aqueous ammonia, or by prolonged treatment with ammonia-gas and subsequent standing (Boullay). — On boiling the product (from olive oil) with water, a milky frothing liquid is obtained, on the surface of which the amide collects in a solid form on cooling. The acid mother-liquor contains glycerin, colouring matter, an acid compound of a non-fatty acid with ammonia, and a little margarate and stearate of ammonia (Boullay).

*Preparation.* A mixture of 1 volume almond oil, 2 volumes alcohol, and 4 volumes concentrated ammonia, is allowed to stand in a closed vessel, with occasional shaking, for several months, or until it solidifies ; the mass is then collected, pressed, and purified by washing and re-crystallisation. — Carlet employs 1 volume of hazel-nut oil and 1 to 2 volumes of a saturated alcoholic solution of ammonia, and allows the mixture to stand until the solid mass is soluble in all proportions in hot alcohol. It is then purified by re-crystallisation from alcohol till the melting-point remains constant.

Crystalline nodules, which begin to melt at 79°, become perfectly fluid at 81°, and solidify to a semi-transparent mass at 78° (Rowney). After melting, it solidifies to a very crystalline mass at 75° (Carlet).

| | | | | | | Rowney. mean. | | Carlet. mean. |
|---|---|---|---|---|---|---|---|---|
| 36 C | 216 | ........ | 76·86 | ........ | 76·48 | ........ | 76·43 |
| N | 14 | ........ | 4·98 | ........ | 4·59 | ........ | 5·07 |
| 35 H | 35 | ........ | 12·45 | ........ | 12·27 | ........ | 12·63 |
| 2 O | 16 | ........ | 5·71 | ........ | 6·66 | ........ | 5·87 |
| C³⁶NH³⁵O² | 281 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Bouillay's margaramide, obtained from olive oil and melting at 60°, contained 75·72 p. c. C., 5·32 N., 12·96 H., and 6·00 O.

Oleamide acquires a yellow colour and a rancid odour in the air. — When heated with alcoholic *potash* in a sealed tube, it is decomposed with formation of oleate (Carlet). It is not attacked by boiling solution of caustic potash, but is decomposed by the fused hydrate (Rowney).

Insoluble in *water ;* easily soluble in warm *alcohol* (Rowney).

## Elaïdamide.

$$C^{36}NH^{35}O^2 = C^{36}AdH^{33},O^2.$$
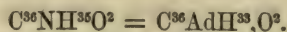
Th. Rowney. *Trans. Roy. Soc. Edin.* 21, part 2 ; *Chem. Gaz.* 1855, 361, *J. pr. Chem.* 67, 157 ; abstr. *Lieb. Kopp. Jahresb.* 1854, 465 ; 1855, 531 ; Prelim. notice : *Chem. Soc. Qu. J.* 7, 200.

Elaïdin, obtained by the action of hyponitric acid on almond oil, is allowed to stand in a close vessel with 4 times its volume of ammonia-water and twice its volume of alcohol ; and the amide, which is formed in abundance, is collected, pressed, and purified by washing and recrystallisation.

Shining, colourless needles, which melt partially at 92° and completely at 94°, and solidify to an opaque mass at 91°.

| | | | | | | Rowney. mean. |
|---|---|---|---|---|---|---|
| 36 C | 216 | ........ | 76·86 | ........ | 76·44 |
| N | 14 | ........ | 4·98 | ........ | 4·88 |
| 35 H | 35 | ........ | 12·45 | ........ | 12·70 |
| 2 O | 16 | ........ | 5·71 | ........ | 5·98 |
| $C^{36}NH^{35}O^2$ | 281 | ........ | 100·00 | ........ | 100·00 |

Isomeric with oleamide.

## Primary Nucleus, $C^{36}H^{36}$.

## Stethal.

$$C^{36}H^{36}O^2 = C^{36}H^{36}, H^2O^2.$$
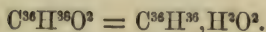
Not obtained in the pure state. — Occurs in spermaceti. See xvi, 344.

## Stearic Acid.

$$C^{36}H^{36}O^4 = C^{36}H^{36}, O^4.$$
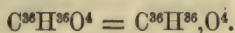
CHEVREUL. *Ann. Chim.* 88, 225; *Schw.* 14, 420; *Ann. Chim. Phys.* 2, 354. — *Ann. Chim. Phys.* 23, 19; *Schw.* 39, 175. — *Recherches sur les corps gras.*
BRACONNOT. *Ann. Chim.* 93, 250.
REDTENBACHER. *Ann. Pharm.* 35, 46.
BROMEIS. *Ann. Pharm.* 35, 86; 37, 303.
STENHOUSE. *Ann. Pharm.* 36, 57.
ERDMANN. *J. pr. Chem.* 25, 497.
FRANCIS. *Ann. Pharm.* 42, 256; *Phil. Mag.* 21, 161.
GOTTLIEB. *Ann. Pharm.* 57, 35.
LAURENT & GERHARDT. *Compt. rend.* 28, 400; *Compt. chim.* 1849, 337; *Ann. Pharm.* 72, 272.
HARDWICK. *Chem. Soc. Qu. J.* 2, 232; *Ann. Pharm.* 72, 268.
CROWDER. *Phil. Mag.* [4] 4, 21; *J. pr. Chem.* 57, 292; *Pharm. Centr.* 1853, 2.
HEINTZ. See references xvi, 343.
BERTHELOT. See references xvi, 350.
PEBAL. *Wien. Akad. Ber.* 13, 285; *Ann. Pharm.* 91, 138; *J. pr. Chem.* 63, 385; *Chem. Centr.* 1854, 810.

‒ *Talgsäure.* — *Acide stéarique.* See the other synonyms, xvi., 365, 366 — *History*, xvi, 350.

*Occurrence.* As tristearin, more especially in the solid fats. (See xvi, 385.)

The following sources of stearic acid must also be noticed. In spermaceti combined with ethal or similar compounds (xvi, 347). — In

the *Mineral-moor* of Marienbad (Lehmann, *J. pr. Chem.* 65, 481). In
sweat (Schottin, *Pharm. Viertelj.* 2, 57). See also *Cerotic acid.*

*Formation.* 1. By the saponification of tristearin. — 2. By heating
stethal (xvi, 347) with potash-lime (Heintz). — According to Lewy
(*Compt. rend.* 16, 677) and Gerhardt by heating cerin with potash-
lime, but according to Brodie not. (See under *Cerotic acid.*)

*Preparation.* According to Chevreul (xvi, 355); Heintz (xvi, 354).
Its preparation in the pure state is more difficult by Chevreul's method;
in Heintz's process, on the other hand, ethers of the fatty acids are
apt to be formed (Berthelot, *N. Ann. Chim. Phys.* 41, 220). Pebal
proceeds in the same way as Heintz, but employs neutral acetate of
lead for the fractional precipitation; precipitates at the boiling heat;
and boils the precipitates with the liquid for ten minutes; even thus,
however, pure stearic acid is obtained only after very often repeated
fractional precipitation. — Stearic acid is most easily obtained pure from
mutton suet. The suet is saponified with $\frac{1}{4}$th to $\frac{1}{3}$rd its weight of
caustic potash; the soap is decomposed with boiling hydrochloric
acid; and the fatty acids are washed, dissolved in a little hot alcohol,
and allowed to crystallise, then pressed, and repeatedly recrystallised
from a relatively large quantity of alcohol till the melting-point
reaches 69·1 to 69·2° (Heintz). The expressed fat of *Cocculus indicus,*
treated in the same way, yields pure stearic acid (Crowder). — Shea-
butter (xvi, 386) is the material best adapted for the preparation of
stearic acid (H. L. Buff, Oudemanns). It contains about 70 p. c. of
stearic to 30 p. c. of oleic, but no other solid fatty acid (Oudemanns,
*J. pr. Chem,* 89, 215).

*Properties.* Stearic acid crystallises from alcohol in nacreous
needles and laminæ (Chevreul); in laminæ (Heintz). It melts at 69·1°
to 69·2° to a colourless oil, which on cooling solidifies to a white, fine,
scaly crystalline mass, lamino-crystalline on the recently fractured
surface (Heintz). The impure acid solidifies in masses of acicular or
wavellitic structure. The melting point was found by Chevreul at 75°
(solidifying point 70°); by Duffy, at 68° (solidifying point 65·8°);
by Stenhouse, at 69°; by Redtenbacher, Kopp, and others at 70°; by
Hardwick, at 70·5°; Pebal found that the purest acid melted at 69·2°.
— After fusion it is friable and greasy to the touch (Chevreul). It
expands very strongly when heated, especially at the moment of fusion
(about 11 p. c.), and contracts so strongly in solidifying that cast
lumps appear porous. Its volume, that at 0° being taken for unity, is
1·038 at 50°, 1·054 at 60°, 1·079 at 70°, and by fusion the volume at 70°
increases to 1·198. Between 9° and 11° its specific gravity is equal to
that of water (H. Kopp, *Ann. Pharm.,* 93, 184). It boils and distils
in a vacuum (Chevreul), and in quantities of 15 to 20 grammes under
the ordinary atmospheric pressure, for the most part without alteration
(Laurent and Gerhardt, Hardwick, Heintz). When heated to 300
— 330° in a sealed tube for several hours, it does not alter either its
appearance or its melting-point, or give off either gas or water
(Berthelot). It is tasteless and inodorous, reddens litmus when warm,
and even when cold if it be dissolved in strong alcohol, but on adding
water, which precipitates the acid, the blue colour is restored
(Chevreul). It has a distinct acid reaction (Heintz).

| | | Chevreul. | Redten-bacher. | Sten-house. | Erd-mann. | Hard-wick. | Francis. |
|---|---|---|---|---|---|---|---|
| 36 C .................. | 216 | 76·06 | 76·30 | 75·51 | 75·75 | 76·50 | 76·13 | 74·73 |
| 36 H.................. | 36 | 12·68 | 12·43 | 12·86 | 12·78 | 12·81 | 12·86 | 12·46 |
| 4 O .................. | 32 | 11·26 | 11·27 | 11·63 | 11·47 | 10·69 | 11·01 | 12·81 |
| $C^{36}H^{36}O^4$ ............ | 284 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

Laurent and Gerhardt.

| | Crowder. | Gottlieb. | a. | b. | Heintz. | Pebal. |
|---|---|---|---|---|---|---|
| C .... | 75·91 .... | 76·29 .... | 75·41 .... | 75·60 .... | 75·57 to 75·88 .... | 75·84 to 76·15 |
| H .... | 13·01 .... | 12·83 .... | 12·53 .... | 12·61 .... | 12·59    12·85 .... | 12·83    12·71 |
| O .... | 11·08 .... | 10·88 .... | 12·06 .... | 11·79 | | |

100·00 .... 100·00 .... 100·00

The formulæ $C^{35}H^{35}O^{3\cdot5}$ (Chevreul), $C^{68}H^{68}O^7$ (Redtenbacher, Erdmann), $C^{68}H^{66}O^7$ (Stenhouse), $C^{38}H^{38}O^4$ (Gerhardt) have been successively proposed for stearic acid. Laurent and Gerhardt gave the formula $C^{34}H^{34}O^4$, according to which stearic acid would be isomeric with margaric acid. The above formula first proposed by Hardwick for stearic acid separated from bassia-oil (bassic acid), then adopted by Crowder for the stearophanic acid of Francis, has been recognised by Heintz as the true formula of stearic acid.

*Decompositions.* 1. When 90 grms. of stearic acid are subjected to dry distillation, the greater part passes over unchanged, but a smaller portion is resolved into carbonic acid, water, and stearone; the distillate likewise contains acetic acid, butyric acid, a fatty acid of lower melting point than stearic acid, also hydrocarbons of the formula $C^n H^n$, and ketones richer in oxygen than stearone,—these, as well as the hydrocarbons, probably resulting from further decomposition of the stearone. The black-brown residue in the retort still contains stearone, but scarcely any fatty acids (Heintz).

Chevreul found in the distillate 96 p. c. of unaltered stearic acid, small quantities of volatile acid, and brown empyreumatic oil, with traces of acetic and sebacic acids; carbonic acid and hydrocarbons were likewise given off during the distillation. According to Redtenbacher, no sebacic acid is produced, the formation of that acid taking place only when oleic acid is present; but, in addition to a fatty acid melting at 60—61° (regarded by Redtenbacher as margaric acid) there are likewise obtained margarone (see under *Stearone*) and an empyreumatic oil. If the fatty acid be combined with lime, the lime-salt exhausted with ether, the margarone allowed to crystallise out as much as possible, and the ether evaporated, the empyreumatic oil remains behind. This oil, when purified by rectification, contains on the average 83·96 p. c. C. and 14·19 H. It must, therefore, be regarded as a hydrocarbon, but mixed with the ketone of an acid of lower atomic weight than stearic acid (Heintz). The solid distillate was mixed with hydrate of lime to a soap, and this was washed with ether, which left stearate of lime together with a small quantity of the lime-salt of a more fusible acid. The ether, when distilled, deposited stearone, then a soft, greasy mixture, and ultimately there remained an oil which solidified a little above 0°. Of this oil, one portion (*a*) passes off in distillation between 273° and 293°, a second portion (*b*) between 293° and 309°, and the residue in the retort is solid at medium temperatures. The portion *a* deposits a few laminæ at 0°, *b* a considerable quantity; the latter contains on the average 84·94 p. c. C.,

14·20 H., and 0·86 O., and is therefore a mixture of hydrocarbons $C^nH^n$, and ketones (Heintz).

2. Stearic acid mixed with platinum-black, and heated to 100° in *oxygen gas*, forms carbonic acid, and at 200° is completely converted into carbonic acid and water (Reiset and Millon, *N. Ann. Chim. Phys.* 8, 285 ; *Ann. Pharm.* 48, 199). — Heated in oxygen to 180°, it burns with a dazzling light (Reiset and Millon). It burns in the air like wax (Chevreul). With ozone it behaves like palmitic acid (xvi, 357).

3. Heated with *chromic acid*, sulphuric acid, and water, it yields chromic oxide, and an acid melting at 64—65°, the alcoholic solution of which first deposits unaltered stearic acid, then an acid (Redtenbacher's margaric acid) melting between 59° and 60° (Redtenbacher). — 4. *Permanganate of potash* converts stearic acid into stearate and carbonate of potash (Cloez and Guignet, *Compt. rend.* 46, 1110).

5. *Nitric acid* forms from stearic acid small portions of volatile acids, which mix with the unaltered stearic acid, and lower its melting-point (Heintz). When stearic acid is heated with 2 or 3 pts. nitric acid, violent action takes place after half-an-hour, nitric acid and pungent gases being given off, and the fused acid being converted into a tenacious frothy mass, then becoming clear and mobile, and finally solidifying as it cools to a tallowy mass which melts at 35° to 45°. According to Bromeis, this mass contains margaric acid, $C^{34}H^{34}O^4$ melting-point 60·5° ; 74·05 C., 12·58 ; silver-salt 53·48 C., 8·80 H., 28·22 Ag), and if crude stearic acid has been used, an oil formed from oleic acid, and coloured blood-red by potash (Bromeis, *Ann. Pharm.* 35, 86). After several days' treatment with nitric acid, the stearic acid disappears completely, being converted into suberic and succinic acids (Bromeis). In later experiments Bromeis (*Ann. Pharm.* 37, 303) obtained also azoleic acid (see *Oleic acid*, p. 67). Azelaic acid (p. 80) is not formed from stearic acid.

6. Stearic acid fused with anhydrous *phosphoric acid* forms a yellow mass similar to that obtained in like manner from margaric acid (p. xvi, 357), but less coloured. This body, when freed from the unaltered stearic acid, melts at 54—60°, and contains, on the average, 80·4 p. c. C., 12·9 H., and 6·7 O ($C^{36}H^{34}O^2$ = 81·2 p. c. C., 12·77 H. and 6·03 O), and is converted by hot nitric acid into a brittle waxy mass containing 77·25 p. c. C., 12·22 H. and 10·53 O. (Erdmann, *J. pr. Chem.* 25, 500).

7. Dry *chlorine gas* at 100° converts stearic into chlorostearic acid (Hardwick). — 8. *Bromine* heated with stearic acid and water in a sealed tube, forms a dark brown liquid, which does not alter perceptibly at 100°, but between 130° and 140° is slowly converted into a yellow oily mixture of bromo- and bibromo-stearic acids, mixed with unaltered stearic acid. Formation of bromo-stearic acid :—

$$C^{36}H^{36}O^4 + Br^2 = C^{36}H^{35}BrO^4 + HBr.$$
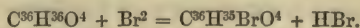
When more than 2 at. bromine is used to 1 at. stearic acid, a large quantity of bibromo-stearic acid is produced, but even then a part of the stearic acid remains unaltered. If the heat is raised above 140° the mass remains brown, or charcoal separates from it (Oudemanns,

*J. pr. Chem.* 89,193). — 9. *Pentachloride of phosphorus* brought in contact with stearic acid at a moderate heat forms a colourless mass, which soon becomes heated to 150°, turning brown and black. When distilled it gives off hydrochloric acid, a small quantity of water, a hydrocarbon, stearic acid, and a solid product less soluble in alcohol than stearic acid (Chiozza, *Gerhardt's Traite*, 2, 851). — 11. Stearate of potash, in contact with *oxychloride of phosphorus*, becomes slightly heated, and at 150° swells up to a dark jelly, perhaps forming chloride of stearyl, inasmuch as the product treated with alcohol yields stearate of ethyl (Pebal). — 12. When stearic acid is heated with an equal weight of *sulphur*, a trace of hydrosulphuric acid is given off, and the same products are formed as when stearic acid is heated by itself (Anderson, *Ann. Pharm.* 63, 373). — 13. The acid heated with *oil of vitriol* to 100°, for several hours, is decomposed, with evolution of sulphurous acid, and carbonises at a higher temperature (Chevreul).

14. Stearate of *lime* subjected to dry distillation, gives off marsh-gas and olefiant gas (or gases having the same composition as the latter), and yields a distillate containing a large quantity of stearone, with small quantities of other ketones, while carbonate of lime remains behind. The distillate does not contain any fatty acid (Heintz). See *Stearone.*

15. Stearic acid distilled with excess of *aniline*, yields phenyl-stearamide (Pebal). On the other hand, stearic acid crystallises unaltered from its alcoholic solution mixed with aniline (Pebal).

16. Stearic acid heated with *methylic, ethylic,* and the *homologous alcohols,* with *quercite, pinite,* and other *carbohydrates,* with *glycerin, orcin, opianyl (meconin) erythroglucin* and *cholesterin,* yields ethereal compounds formed from the acid and the other body, with elimination of water. (For details see the several compounds; on the formation of glycerides, also xvi, 358.) When heated for thirty-six hours with *pyrogallic acid* (xi, 398) to 200°, it forms a crystalline compound (Rösing, *Compt. rend.* 44, 1149 ; *J. pr. Chem.* 71, 325).

*Combinations.* Stearic acid is insoluble in water.

It dissolves partially and without coloration in 10 parts *oil of vitriol* at 20°, the undissolved portion, if left at rest, being converted into needle-shaped crystals ; water added to the solution throws down the stearic acid in white flocks. On heating the liquid, two yellowish layers are formed, the upper containing the larger proportion of stearic acid, and solidifying to a soft mass at 44°, while the lower, when cooled to 12°, slowly deposits the stearic acid in spherules composed of needles ; water also precipitates but a small portion of the stearic acid from it (Chevreul).

*Stearates.* Stearic acid dissolves in a cold aqueous solution of alkaline carbonate, probably from formation of bicarbonate, and does not expel the carbonic and form a mono-acid salt till heated to about 100°. On the other hand, the stearates are decomposed by most other acids, the separated stearic acid rising to the surface as an oil when the liquid is warm. The stearates have the consistence of hard soaps and plasters, and are mostly insoluble in water.

*Stearate of Ammonia.* Stearic acid, either in the fused or the solid

state, al sorbs ammonia gas without elimination of water, the quantity absorbed amounting, after a month, when the absorption ceases, to 6·68 parts ammonia for every 100 parts of acid (1 at $NH^3 = 5·9$ parts). The compound is solid, white, inodorous, has an alkaline taste, may be sublimed in a vacuum, and then gives off ammonia, but takes it up again on cooling. When heated in a vessel containing air, it gives off ammonia and water, and yields a sublimate of acid salt, mixed with empyreumatic oil. The neutral salt, when protected from the air, dissolves in hot water, especially in ammoniacal water, and the solution on cooling deposits the acid salt in nacreous laminæ (Chevreul). The solution of stearic acid in hot dilute aqueous ammonia deposits small needles on cooling. When heated for some time, it becomes turbid, and is then not clarified by further addition of ammonia. The needles dissolve in alcohol and in ether (Crowder).

*Stearate of Potash.* A. *Mono-acid.* — Separates on cooling from a solution of 1 part stearic acid and 1 part hydrate of potash in 10 parts water, in white opaque granules, and may be purified by pressure, solution in 18 parts alcohol of sp. gr. 0·821, and washing the needles which then separate, with cold alcohol (Chevreul). — Obtained also from carbonate of potash and stearic acid in the same manner as myristate of potash (xvi, 212) (Crowder). — Shining, delicate needles, scales, and laminæ, which, when aggregated, form a hard soap; has a faint alkaline taste (Chevreul).

In air saturated with moisture it takes up $\frac{1}{10}$th of its weight of water. One part of the salt forms, with 10 parts of cold water, an opaque gum, which melts at 99° and solidifies to a pearly gum on cooling. One part of the salt dissolves completely in 25 parts of boiling water, forming a liquid which is still limpid at 92°, and solidifies to a pearly mass on cooling.

The solution of 1 part of the salt in 100 parts of hot water deposits on cooling a mixture of mono- and bi-stearate of potash, while one-fourth of the entire quantity of potash remains dissolved. When the solution of the salt in alcohol, or in 20 parts of boiling water, is mixed with 1,000 parts of boiling water, or 5,000 parts of cold water, it deposits all the stearic acid as bi-acid salt, whilst half the potash remains dissolved in the water. In like manner the mono-acid salt, when drenched with 5,000 parts of cold water, gives up half its potash and is converted into a bi-acid salt without forming a gum. In these cases the alkaline water contains a trace of stearic acid in solution (Chevreul). It dissolves at 10° in 231 parts alcohol of sp. gr. 0·794, in 10 parts at 66°, the latter solution becoming turbid at 55°, and solidifying at 38°. It dissolves in 6·7 parts of boiling alcohol of sp. gr. 0·794, forming a liquid which gelatinises on cooling. It dissolves in ether-alcohol, and crystallises therefrom (Crowder, Hardwick). Boiling ether withdraws from the mono-acid salt a certain quantity of stearic acid, leaving a compound richer in potash (Chevreul).

| | | | Chevreul. mean. |
|---|---|---|---|
| $C^{36}H^{35}O^4$ .............. | 275·0 | ........ 85·35 | |
| KO ............ | 47·2 | ........ 14·65 | ........ 15·19 |
| $C^{36}H^{35}KO^4$ ........ | 322·2 | ........ 100·00 | |

B. *Bi-acid.* Chevreul's *matière nacrée*. Formation, *supra;* Preparation

(xvi, 355.) Delicate, white, pearly laminæ, tasteless, softening at 100°. The solution in absolute alcohol reddens litmus on the addition of a little water, while a larger quantity of water restores the blue colour by precipitating the bi-acid salt. — Cold water dissolves in a month a very small quantity of potash, and a trace of stearic acid. The salt dissolves at 245° in 318 parts alcohol of sp. gr. 0·834, in 278 parts of alcohol of sp. gr. 0·794, and in 3·7 parts at the boiling heat. The solution crystallises on cooling, and is precipitated by water, with separation of tri-acid salt. It dissolves partially in boiling ether, the solution on cooling depositing the mono-acid salt, while stearic acid remains dissolved (Chevreul).

| | | | | Chevreul. |
|---|---|---|---|---|
| $C^{72}H^{71}O^7$ ........................ | 559·0 | ........ | 92·22 | |
| KO ........................ | 47·2 | ........ | 7·78 | ........ 8·57 |
| $C^{36}H^{35}KO^4,C^{36}H^{36}O^4$ .... | 606·2 | ........ | 100·00 | |

C. *Triacid* and *Quadracid?* Bistearate of potash forms with 1,000 parts of boiling water a solution of mono-acid salt, rendered turbid and gummy by suspended triacid salt:

$$2(C^{36}H^{35}KO^4,C^{36}H^{36}O^4) = C^{36}H^{35}KO^4,2C^{36}H^{36}O^4 + C^{36}H^{35}KO^4.$$
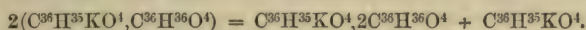
This solution becomes clearer and more fluid at 75°, deposits a few flocks on cooling to 67°, and from 59° to 26° pearly laminæ of the bi-acid salt resulting from decomposition of the mono-acid salt formed at the higher temperature, and mixing with the ter-acid salt. This mixed precipitate contains 6·18 parts potash to 100 parts stearic acid (5 at. stearic acid, 2 at. potash = 6·73 parts); it melts below 100°, and solidifies to a translucent wax at 75° to 71°. Its solution in hot alcohol deposits bi-acid salt on cooling ; on the other hand, when boiled with 1,000 parts of water, it gives up more potash, and is converted into quadrostearate of potash containing 4·47 parts potash to 100 parts acid (calc. 3·9 parts KO), melting to an oil when warmed, and solidifying on cooling to a white mass, which swells up in water (Chevreul).

*Stearate of Soda.* Stearic acid agitated and warmed with disodic phosphate, forms an emulsion which clarifies on cooling from formation of stearate of soda (Marcet, *N. Arch. Ph.* nat. 1, 192 ; Kopp's *Jahresb.* 1858, p. 396).

A. *Mono-acid.* 20 parts stearic acid are heated with 13 parts soda and 300 water; and the granular mass which forms on cooling is pressed, dried in the sun, and crystallised from 25 parts of boiling alcohol (Chevreul). Obtained like myristate of soda (xvi, 212). — Shining laminæ or translucent very hard soap (Chevreul). Crystalline network formed of long prisms having a strong pearly lustre (Francis). Melts above 100° ; tasteless at first, afterwards tastes alkaline (Chevreul).

From air saturated with moisture it absorbs at 6°, in 12 days, 7·5 p. c. water, afterwards not any perceptible quantity. When covered with 600 parts of cold water, it becomes more opaque in 14 days by taking up water, and gives up to the water a trace of potash. With 10 parts water at 90°, it forms a thick, nearly transparent solution, which solidifies to a white mass at 62° ; and this, when heated with 40 parts more water, forms a solution which is still filtrable below 100° ; and when mixed with 2,000 parts more water, deposits the biacid salt on cooling, while half the soda and a trace of stearic acid remain in solu-

tion. It dissolves at 10° in 499 parts alcohol of sp. gr. 0·821, and in 20 parts at the boiling heat; the latter solution becomes turbid at 70°, and solidifies on cooling to a transparent jelly, which afterwards becomes opaque and contracts, from formation of numerous shining crystals. Boiling ether withdraws from the salt a small quantity of stearic acid, together with a trace of soda, and yields a slight deposit on cooling (Chevreul).

| | | | | Chevreul. mean. | Redten-bacher. | Crowder. mean. | Heintz. mean. |
|---|---|---|---|---|---|---|---|
| 36 C | ............... | 216 | .... | 70·58 | 68·50 | | |
| 35 H | ............ | 35 | .... | 11·43 | 11·24 | | |
| 3 O | ............... | 24 | .... | 7·86 | 9·78 | | |
| NaO | ............... | 31 | .... | 10·13 | .... 10·98 | .... 10·48 | .... 10·15 .... 10·08 |
| C$^{36}$H$^{35}$NaO$^4$ | .... | 306 | .... | 100·00 | 100·00 | | |

B. *Biacid.* — The soap prepared from 5 parts hog's-lard and 3 parts soda swells up when heated with a large quantity of water, and on cooling deposits bi-stearate of soda as a translucent jelly. — The solution of the monostearate in 2,000 parts of boiling water is left to cool, and the precipitate is collected, washed with cold water, dried, and crystallised from boiling alcohol. It dries on the filter to a somewhat pearly, white, translucent, tasteless film, more fusible than the monostearate. It is insoluble in water, easily soluble in hot alcohol; the solution reddens litmus, but on adding water, which precipitates the salt, the colour is restored (Chevreul).

| | | | | | Chevreul. |
|---|---|---|---|---|---|
| C$^{72}$H$^{71}$O$^7$ | ......................... | 559 | ........ | 94·75 | |
| NaO | ......................... | 31 | ........ | 5·25 | ........ 5·67 |
| C$^{36}$H$^{35}$NaO$^4$,C$^{36}$H$^{36}$O$^4$ | .... | 590 | ........ | 100·00 | |

*Stearate of Baryta.* — 1. Stearic acid is digested for two hours in a closed vessel with an excess of boiling filtered baryta-water; and the precipitated soap is freed from excess of baryta by decanting the liquid and boiling with water, then by boiling with alcohol, from any stearic acid that may have remained uncombined (Chevreul). — 2. Stearate of soda is precipitated with acetate of baryta, and the precipitate is washed successively with alcohol, water, dilute acetic acid, and hot alcohol (Heintz). Prepared by 1, it is a white fusible tasteless powder; by 2, a micro-crystalline pearly precipitate, not fusible without decomposition. Insoluble in boiling water and in boiling alcohol (Chevreul), and in ether (Crowder).

| | | | | Hardwick. | Crowder. | Heintz. |
|---|---|---|---|---|---|---|
| 36 C | ................. | 216·0 | .... | 61·45 .... 61·03 | .... 61·68 | .... 61·02 |
| 35 H | ................. | 35·0 | .... | 9·96 .... 9·90 | .... 10·31 | .... 9·90 |
| 3 O | ................. | 24·0 | .... | 6·83 .... 6·93 | .... 6·27 | .... 7·52 |
| BaO | ................. | 76·5 | .... | 21·76 .... 22·14 | .... 21·74 | .... 21·56 |
| C$^{36}$H$^{35}$BaO$^4$ | ........ | 351·5 | .... | 100·00 .... 100·00 | .... 100·00 | .... 100·00 |

Chevreul found 22·44 p. c. baryta, afterwards 22·31.

*Stearate of Strontia.* — Prepared like the baryta-salt (1). White fusible tastless powder. Insoluble in water, slightly soluble in boiling alcohol (Chevreul).

| | | | Chevreul. |
|---|---|---|---|
| $C^{36}H^{35}O^3$ ............... | 275 | 84·1 | |
| SrO ............... | 52 | 15·9 | .. ..... 16·34 |
| $C^{36}H^{35}SrO^4$ ........ | 327 | 100·0 | |

*Stearate of Lime.* — Obtained by precipitating chloride of calcium with a boiling solution of stearate of potash, and washing the precipitate with boiling water. White fusible, tasteless powder.

| | | | Chevreul. |
|---|---|---|---|
| | | | *mean.* |
| $C^{36}H^{35}O^3$ ............ | 275 | ........ | 90·76 | |
| CaO ............ | 28 | ........ | 9·24 | ........ 9·96 |
| $C^{36}H^{35}CaO^4$ .... | 303 | ........ | 100·00 | |

*Stearate of Magnesia.* — Prepared like the myristate (xvi, 213). After recrystallisation from alcohol it forms dazzling white flocks made up of microscopic laminæ, which dry up to a light fusible powder (Heintz).

| | | | | Heintz. |
|---|---|---|---|---|
| 36 C ............. ....... | 216 | ....... | 73·20 | ....... 73·00 |
| 35 H................... | 35 | ....... | 11·87 | ....... 11·99 |
| 3 O ..................... | 24 | ....... | 8·14 | ....... 8·46 |
| MgO..................... | 20 | ....... | 6·79 | ....... 6·55 |
| $C^{36}H^{35}MgO^4$ .... | 295 | ....... | 100·00 | ....... 100·00 |

*Stearate of Lead.* — Stearic acid heated with 9 parts lead-oxide loses 3·4 p. c. water (Chevreul). 1 at. = 3·17 p. c.

A. *Biplumbic.* Stearic acid is boiled in a close vessel with terplumbic acetate, and the resulting white, transparent, friable soap, which is liquid at 100°, is boiled first with water, then with alcohol (Chevreul).

| | | | Chevreul. |
|---|---|---|---|
| $C^{36}H^{35}O^3$......................... ... | 275 | ....... | 55·11 | |
| 2PbO ............................ | 224 | ....... | 44·89 | ....... 45·58 ........ 46·0 |
| $C^{36}H^{35}PbO^4,PbO$ ........ | 499 | ....... | 100·00 | |

B. *Monoplumbic.* — Obtained by precipitating nitrate of lead with a boiling solution of monopotassic stearate (Chevreul). Heintz proceeds as in the preparation of the myristate (xvi, 313). Redtenbacher precipitates neutral lead-acetate mixed with acetic acid, with an alcoholic solution of the soda-salt. — Fine, amorphous, white powder, melting at about 125° to a colourless liquid, which solidifies to an opaque, amorphous mass (Heintz). Insoluble in ether (Gusserow).

| | | | | Redtenbacher. | | Heintz. |
|---|---|---|---|---|---|---|
| | | | | | | *mean.* |
| 36 C ............... | 216·0 | ....... | 55·87 | ....... | 55·15 | ....... 55·61 |
| 35 H ............... | 35·0 | ....... | 9·05 | ....... | 8·96 | ....... 9·03 |
| 4 O ............... | 32·0 | ....... | 8·28 | ....... | 8·46 | ....... 8·41 |
| Pb ............... | 103·8 | ....... | 26·80 | ....... | 27·43 | ....... 26·95 |
| $C^{36}H^{35}PbO^4$ .... | 386·8 | ....... | 100·00 | ....... | 100·00 | ....... 100·00 |

Chevreul found 29·47 p. c. lead oxide (calc. 28·94 p. c. PbO).

*Stearate of Copper.* — Light-blue bulky amorphous powder. Melts when heated to a green liquid, easily decomposing at the same time (Heintz).

| | | | | | | | | Heintz. |
|---|---|---|---|---|---|---|---|---|
| 36 C | .................... | 216 | ........ | 68·64 | ........ | 68·45 |
| 35 H | ................ | ·35 | ........ | 11·12 | ........ | 11·20 |
| 3 O | .................... | 24 | ........ | 7·63 | ........ | 7·79 |
| CuO | .................... | 40 | ........ | 12·61 | ........ | 12·56 |
| $C^{36}H^{35}CuO^4$ | ........ | 315 | ........ | 100·00 | ........ | 100·00 |

*Mercurous Stearate.* — Obtained by heating mercurous oxide with stearic acid. From mercurous nitrate stearate of potash throws down a white precipitate, which turns grey when dry, and contains 42·52 p. c. mercurous oxide (1 at. = 43·06 p. c. $Hg^2O$). Melts when heated and then decomposes. Insoluble in water; insoluble also in cold alcohol, sparingly soluble in boiling alcohol, easily in ether whether cold or at the boiling heat (Harff).

*Mercuric Stearate.* — Obtained by heating mercuric oxide with stearic acid to 100°, with agitation, or by mixing mercuric nitrate with stearate of potash, in which case it is precipitated in flocks. White, softening between the teeth. Contains 29·19 p. c. mercuric oxide (1 at. = 28·2 p. c. $HgO$). Insoluble in water, sparingly soluble in boiling alcohol, soluble in ether whether cold or boiling (Harff).

*Stearate of Silver.* — Obtained by adding a solution of 20 grms. of the soda-salt in 5 or 6 oz. of strong alcohol to a solution of 12 to 13 grms. silver-nitrate in an equal quantity of alcohol (Crowder). Amorphous, white precipitate, very loose and strongly electric when dry. Assumes a purple colour when exposed to light in the moist state; not altered by light when dry. Insoluble in water, alcohol and ether, easily soluble in aqueous ammonia.

| | | | Redten-bacher. | Hard-wick. | | Francis. | Crowder. | Heintz. |
|---|---|---|---|---|---|---|---|---|
| 36 C | 216 | .... | 55·24 .... | 54·30 .... | 54·82 .... | 53·72 .... | 55·53 .... | 54·90 |
| 35 H | 35 | .... | 8·95 .... | 9·01 .... | 9·08 .... | 8·83 .... | 9·15 .... | 9·03 |
| 4 O | 32 | .... | 8·19 .... | 8·08 .... | 8·49 .... | 8·60 .... | 7·76 .... | 8·45 |
| Ag | 108 | .... | 27·62 .... | 28·61 .... | 27·61 .... | 28·85 .... | 27·56 .... | 27·62 |
| $C^{36}H^{35}AgO^4$ | 391 | .... | 100·00 .... | 100·00 .... | 100·00 .... | 100·00 .... | 100·00 .... | 100·00 |

Contains 28·64 p. c. silver (Laurent and Gerhardt); 27·54 p. c. (Pebal).

Stearic acid dissolves in liquid *carbonic acid* (Gore, *Chem. Soc. Qu. J.*, 15, 163).

Stearic acid dissolves in 40 parts of cold *alcohol* of sp. gr. 0·794, and in any quantity of boiling alcohol of the same strength (Chevreul, Braconnot). The hot solution of 1 part stearic acid in 1 part alcohol of sp. gr. 0·794, becomes turbid at 50°, depositing nacreous scales, and solidifies at 45° (Chevreul).

It dissolves in 8·3 parts cold *ether*, and in all proportions of hot ether (Braconnot); in 3½ parts *bisulphide of carbon*, and in 4·55 parts of benzene of sp. gr. 0·887, at 23° (A. Vogel, *Dingl. pol. J.*, 164, 221).

*Stearic Acid with Lauric, Myristic, Palmitic and Margaric Acids.* — Mixtures of these acids, as shown by Gottlieb for mixtures of stearic and

Chevreul's margaric acid (comp. *Ann. Pharm.* 57, 37), exhibit the relations indicated at page 214, vol. xvi., and the melting points given in the following tables :—

## ACCORDING TO HEINTZ.

### 1. *Stearic and Lauric Acids* (xv, 43).

A mixture of :—

| Stearic acid. | Lauric acid. | Melts at | Mode of Solidifying. |
|---|---|---|---|
| 10 | 90 | 41·5° | Non-crystalline. |
| 20 | 80 | 38·5 | Non-crystalline, warty. |
| 30 | 70 | 43·4 | Small shining crystalline facets on the surface. |
| 40 | 60 | 50·8 | Warty, non-crystalline. |
| 50 | 50 | 55·8 | Scarcely crystalline, slightly granular. |
| 60 | 40 | 59·0 | More distinctly granular; commencement of scaly crystallisation. |
| 70 | 30 | 62·0 | Somewhat more distinctly granulo-scaly. |
| 80 | 20 | 64·7 | Distinctly scaly-crystalline. |
| 90 | 10 | 67·0 | The same. |

### 2. *Stearic and Myristic Acids.* (xvi. 209).

A mixture of :—

| Stearic acid. | Myristic acid. | Melts at | Mode of Solidifying. |
|---|---|---|---|
| 10 | 90 | 51·7° | Non-crystalline, opaque. |
| 20 | 80 | 47·8 | Indistinctly crystalline. |
| 30 | 70 | 48·2 | Lamino-crystalline. |
| 40 | 60 | 50·4 | Beautifully broad-laminar. |
| 50 | 50 | 54·5 | Non-crystalline, opaque. |
| 60 | 40 | 59·8 | Neither needles nor laminæ ; commencement of scaly crystallisation. |
| 70 | 30 | 62·8 | More distinctly scaly. |
| 80 | 20 | 65·0 | Still more distinctly scaly. |
| 90 | 10 | 67·1 | Scaly crystalline. |

### 3. *Stearic and Palmitic Acids* (xvi. 350.)

A mixture of :—

| Stearic acid. | Palmitic acid. | Melts at | Solidifies at | Mode of Solidifying. |
|---|---|---|---|---|
| 90 | 10 | 67·2° | 62·5° | Scaly-crystalline. |
| 80 | 20 | 65·3 | 60·3 | Finely aciculo-crystalline. |
| 70 | 30 | 62·9 | 59·3 | The same. |
| 60 | 40 | 60·3 | 56·5 | Rough, non-crystalline. |
| 50 | 50 | 56·6 | 55·0 | Broad, lamino-crystalline. |
| 40 | 60 | 56·3 | 54·5 | The same. |
| 35 | 65 | 55·6 | 54·3 | Non-crystalline, wavy, shining. |
| 32·5 | 67·5 | 55·2 | 54·0 | The same. |
| 30 | 70 | 55·1 | 54·0 | Non-crystalline, wavy, dull. |
| 20 | 80 | 57·5 | 53·8 | Scarcely acicular. |
| 10 | 90 | 60·1 | 54·5 | Beautifully acicular. |

4. *Stearic, Palmitic, and Myristic acids.*

The melting point of a mixture of 32·5 p.c. palmitic acid with 67·5 p.c. myristic acid, which is situated at 46·2°, sinks lower when to 20 parts of this mixture there are added from 1 to 7 parts of stearic acid. The melting points of the several mixtures are as follows :—

With 1 part stearic acid the melting point is 45·2°
      2      ,,            ,,      44·5
      3      ,,            ,,      44·0
      4      ,,            ,,      43·8
      5      ,,            ,,      44·6
      6      ,,            ,,      45·4
      7      ,,            ,,      46·0
      8      ,,            ,,      46·5

These mixtures solidify to non-crystalline masses (Heintz).

5. *Stearic and Margaric acids* (xvi, 472). Mixtures of these two acids melt more easily than stearic acid, but only a few of them less easily than margaric acid. They solidify almost in the same manner as unmixed fatty acids, differing, therefore, in this respect from mixtures of stearic with palmitic acid (Heintz).

A mixture of :—

| Stearic acid. | Margaric acid. | Melts at | Mode of Solidifying. |
|---|---|---|---|
| 10 | 90 | 59·5° | Scaly crystalline. |
| 20 | 80 | 59·8 | The same, but less distinctly. |
| 30 | 70 | 60·8 | Like the last. |
| 40 | 60 | 61·2 | The same. |
| 50 | 50 | 62·0 | The same, but less pearly. |
| 60 | 40 | 63·1 | The same. |
| 70 | 30 | 64·7 | The same. |
| 80 | 20 | 66·2 | The same. |
| 90 | 10 | 67·6 | Scaly crystalline. |

*Conjugated Compounds of the Primary Nucleus* C³⁶H³⁶.

## Stearate of Methyl.

$$C^{38}H^{38}O^4 = C^2H^3O,C^{36}H^{35}O^3.$$
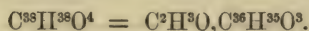
LASSAIGNE. *Ann. Pharm.* 23, 169.
HANHART. *Compt. rend.* 47, 230; *J. pr. Chem.* 77, 5.

*Methylic Stearate. Methyl-stearic ether. Stearinsäure-Methyläther. Talg-holzäther. Stearinformester.*

1. Obtained by heating 1 part of wood-spirit with 1 part oil of vitriol and ½ part stearic acid. — 2. By heating stearic acid with wood-spirit to 200°, in a sealed tube for a day. Purified like the glycerides (xvi, 358). — Melts at 38°. Neutral (Hanhart).

## Stearate of Ethyl.

$$C^{40}H^{40}O^4 = C^4H^5O, C^{36}H^{35}O^3.$$
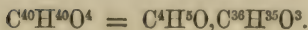
LASSAIGNE. *J. Chim. méd.* 13, 369 ; *Ann. Pharm.* 23, 168.
REDTENBACHER. *Ann. Pharm.* 35, 51.
STENHOUSE. *Ann. Pharm.* 36, 58.
FRANCIS. *Ann. Pharm.* 42, 261.
CROWDER. *Phil. Mag.* [4], 21 ; *J. pr. Chem.* 57, 292.
HEINTZ. See memoirs cited, xvi., 343.
DUFFY. *Chem. Soc. Qu. J.*, 5, 197 ; *Ann. Pharm.* 88, 291.
PEBAL. *Ann. Pharm.* 91, 153.
BERTHELOT. See memoirs cited, xvi., 350.
HANHART. *Compt. rend.* 47, 230 ; *Chem. Centr.* 1858, 676 ; *J. pr. Chem.*
    77, 5.
BERTHELOT and FLEURIEN. *N. Ann. Chim. Phys.* 67, 79 ; *Compt. rend.*
    51, 1020 ; *Ann. Pharm. Suppl.* 1, 271 ; *Chem. Centr.* 1861, 230.

*Ethylic Stearate. Ethyl-stearic ether. Talgäther. Stearinsaures Aethyloxyd.*
*Stearin-säurevinester. Stearophansaure-äther.*

*Formation.* 1. By heating stearic acid with alcohol to 200°, small
quantities are produced also heating the materials together to 100° for
102 hours (Berthelot); or by boiling stearic acid with alcohol (Lassaigne).
— 2. By passing hydrochloric acid gas into an alcoholic solution of stearic
acid (Redtenbacher); by heating alcoholic stearic acid with acetic acid
to 100°, the whole of the stearic acid then entering into combination in
102 hours (Berthelot). — By the action of alcohol on the product formed
by heating stearic acid with pentachloride of phosphorus (Pebal). —
4. By boiling tristearin with a solution of sodium in absolute alcohol
(Duffy), or by heating tristearin with small quantities of alcoholic potash
(Bouis, *Compt. rend.*, 45, 35).

*Preparation.* Hydrochloric acid gas is passed into alcoholic stearic
acid ; the mass which solidifies on cooling is dissolved in boiling alcohol ;
the solution poured into a boiling dilute aqueous solution of carbonate
of soda ; and the stearic ether which separates on cooling is purified by
repeated solution in boiling alcohol, and precipitation with a small
quantity of water (Heintz). The ether produced by heating stearic acid with
alcohol to 200° in a sealed tube for several days, may be purified like palmitin (xvi.,
337) (Hanhart).

*Properties.* Crystalline mass, semi-transparent, and resembling white
wax. Melts at 33·7° (Duffy, Heintz); at 27° (Lassaigne) ; 30°—31° (Redten-
bacher) ; 31° (Hanhart) ; 32° (Francis) ; 32·9° (Pebal) ; 33·3 (Crowder). Solidifies
to a translucent mass (Duffy); to a crystalline mass, soft at first, after-
wards becoming hard and brittle (Heintz). Volatilises a little at the
heat of the water-bath (Crowder); boils at 224° with partial decompo-
sition, leaving a residue of charcoal (Duffy). Tasteless ; melts on the
tongue, producing a sensation of cold (Crowder) ; has a buttery taste
(Francis). Inodorous in the cold ; smells faintly when heated (Francis).

|  |  |  |  |  |  | Redtenbacher. |  | Stenhouse. |
|---|---|---|---|---|---|---|---|---|
| 40 C | .......................... | 240 | ........ | 76·92 | ........ | 76·13 | ..... ,. | 76·30 |
| 40 H | .......................... | 40 | ........ | 12·82 | ........ | 12·85 | ........ | 12·92 |
| 4 O | .......................... | 32 | ........ | 10·26 | ..... ... | 11·02 | ........ | 10·78 |

$C^4H^5O,C^{36}H^{35}O^3$ ........ 312 ....... 100·00 ......... 100·00 ........ 100·00

| Francis. |  | Crowder. |  | Duffy. |  | Pebal. |  | Heintz. |
|---|---|---|---|---|---|---|---|---|
| 76·20 | ............ | 76·90 | ........ | 76·53 | ........ | 76·79 | ...,.... | 76·59 |
| 12·77 | ............ | 13·23 | ........ | 12·50 | . ...... | 12·91 | ........ | 12·84 |
| 11·03 | ............ | 9·87 | ........ | 10·97 | ........ | 10·30 | ........ | 10·57 |
| 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | ....,.... | 100·00 |

*Decompositions.* 1. For the decomposition by heat, see above. — 2. By water at 100° it is partially resolved in 102 hours into alcohol and stearic acid, more abundantly by a mixture of 1 vol. acetic acid and 2 to 3 water, the latter reaction taking place without any formation of acetic ether (Berthelot). — 3. Fuming *hydrochloric acid* at 100°; converts it in 106 hours into chloride of ethyl and stearic acid (Berthelot). — 4. Decomposed by alcoholic, but not by aqueous *potash* (Duffy). — 5. Anhydrous *baryta* heated with the ether to 200° in a sealed tube, decomposes it completely, and the product heated with water yields alcoholate and stearate of baryta:

$$C^{40}H^{40}O^4 + 2BaO = C^{36}H^{35}BaO^4 + C^4H^5BaO^2.$$
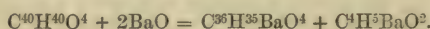
These are the only products ; no ethylic ether is formed(Berthelot and Fleurien). — 6. Heated to 100° with *glycerin*, it does not yield stearin, not even in presence of hydrochloric acid (Berthelot).

Stearate of ethyl dissolves very easily in *alcohol* and in *ether*, and crystallises from alcohol, but not from ether (Duffy).

## Bistearate of Ethylene.

$$C^{76}H^{74}O^8 = C^4H^4O^2,2C^{36}H^{35}O^3.$$
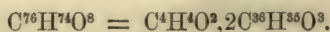
WURTZ.   *N. Ann. Chim. Phys.* 55, 436.

*Ethylenic* or *Glycolic Bistearate. Glycol distéarique. Distearinglycolester.*

Obtained by the action of bromide of ethylene (viii, 366) on stearate of silver. The product is exhausted with ether, the ethereal solution treated with potash-hydrate, and the filtrate left to evaporate.

Light, shining laminæ, melting at 76°, and resembling tristearin.

|  |  |  |  |  |  | Wurtz. |
|---|---|---|---|---|---|---|
| 76 C | .............................. | 456 | ........ | 76·76 | ........ | 76·25 |
| 74 H | .............................. | 74 | ........ | 12·46 | ........ | 12·69 |
| 8 O | ......... ............... | 64 | ........ | 10·78 | ........ | 11·06 |

$C^4H^4O^2,2C^{36}H^{25}O^3$ ........ 594 ........ 100·00 ........ 100·00

## Monostearin.

$$C^{42}H^{42}O^8 = C^6H^7O^5,C^{36}H^{35}O^3.$$
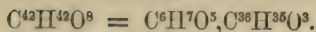
BERTHELOT. *Chim. organ.* 2, 65 ; *Ann. Chim. Phys.* 41, 221.

A mixture of equal parts of stearic acid and glycerin is heated to 200° in a sealed tube for 36 hours, then left to cool. On opening the tube there is found floating on the excess of glycerin, a solid layer, containing monostearin and uncombined stearic acid. This layer is melted, mixed with a small quantity of ether, then with slaked lime, and heated to 130° for a quarter of an hour, whereby the stearic acid is made to unite with lime. The monostearin is obtained by exhaustion with ether and spontaneous evaporation. A mixture of stearic acid and glycerin enclosed in a sealed tube and left to itself for three months at ordinary temperatures, likewise yields very small quantities of glycerin.

*Properties.* Very small white needles, aggregated in roundish grains, melting at 61°, and solidifying at 60° to a hard, friable, waxy mass. Neutral in alcoholic solution. Volatilises without decomposition in a vacuum.

|  |  |  |  |  | Berthelot. |
|---|---|---|---|---|---|
|  |  |  |  |  | *mean.* |
| 42 C | 252 | .... ...... | 70·4 | ............ | 70·4 |
| 42 H | 42 | ............ | 11·7 | ............ | 12·3 |
| 8 O | 64 | ............ | 17·9 | ............ | 17·3 |
| $C^6H^7O^5,C^{36}H^{35}O^3$ | 358 | ............ | 100·0 | ............ | 100·0 |

*Decompositions.* Monostearin decomposes when *heated* in a tube, with formation of acrolein. — When it is heated on platinum-foil, a portion evaporates, while the rest turns yellow, and *burns* with a white, very luminous flame. Heated with fuming *hydrochloric acid* to 100° in a sealed tube for 110 hours, it is almost wholly resolved into glycerin and stearic acid. A trace of a neutral chlorinated liquid is formed at the same time. — Monostearin is decomposed by heating for some hours to 100°, with moist *protoxide of lead,* yielding nearly 25 p.c. glycerin (calc. 25·56 p.c., $C^6H^8O^6$). — It is not decomposed by heating to 100° for 26 hours with alcoholic *acetic acid.*

Very slightly soluble in cold *ether.*

## Distearin.

$$C^{76}H^{78}O^{12} = C^6H^8O^6,2C^{36}H^{35}O^3.$$
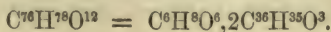
BERTHELOT. *Chim. organ.* 2, 67 ; *N. Ann. Chim. Phys.* 41, 226.

*Formation and Preparation.* 1. One part of monostearin is heated with 3 parts of stearic acid to 260° for three hours. — 2. Stearic acid is heated with an equal quantity of glycerin to 100° for 114 hours, or to

275° for seven hours. — 3. The stearin of natural fats is heated with excess of glycerin to 200° for 22 hours. Separated like monostearin (p. 117).

White microscopic laminæ, which melt at 58°, and solidify like monostearin, at 55°. Obtained in needles by spontaneous evaporation from ether. Neutral.

Decomposible by moist oxide of lead, at 100°.

|  |  |  |  |  | Berthelot. |
|---|---|---|---|---|---|
| 78 C | ............................ | 468 | ........ | 72·9 | ........ 72·0 to 73·8 |
| 78 H | ............................ | 78 | ........ | 12·1 | ........ 12·2 „ 12·5 |
| 12 O | ............................ | 96 | ........ | 15·0 |  |
| $C^6H^8O^6,2C^{36}H^{35}O^3$ | ........ | 642 | ........ | 100·0 |  |

## Tristearin.

$$C^{114}H^{110}O^{12} = C^6H^5O^3,3C^{36}H^{35}O^3.$$
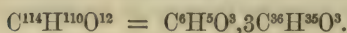
CHEVREUL.   *Recherches sur les corps gras.*
BRACONNOT.   *Ann. Chim.* 93, 225.
A. VOGEL.   *Ann. Chim.* 58, 154.
LECANU.   *Ann. Chim. Phys.* 55, 192; *J. Pharm.* 20, 323; *Ann. Pharm.* 12, 25; abstr. *Pogg.* 31, 638.
LIEBIG & PELOUZE.   *Ann. Pharm.* 19, 264.
REDTENBACHER.   *Ann. Pharm.* 35, 195.
FRANCIS.   *Ann. Pharm.* 42, 254; *Phil. Ann.* 21, 161.
ARZBÄCHER.   *Ann. Pharm.* 70, 239; *Pharm. Centr.* 1849, 585.
HEINTZ.   See memoirs already cited (xvi, 343, 344, Nos. 1, 2, 5, and 9).
DUFFY.   *Chem. Soc. Qu. J.,* 5, 197; *J. pr. Chem.* 57, 335; abstr. *Ann. Pharm.* 84, 291; *Lieb. Kopp. Jahresb.* 1852, p. 507. — *Chem. Soc. Qu. J.,* 5, 303; *J. pr. Chem.* 58, 358; *Lieb. Kopp. Jahresb.* 1852, p. 511.
BERTHELOT.   See memoirs already cited. — *Chim. organ.* 2, 52, et seq.
H. KOPP.   *Ann. Pharm.* 93, 194; *Lieb. Kopp. Jahresb.* 1855; p. 43.
BOUIS.   *Compt. rend.* 45, 35; *J. pr. Chem.* 72, 308; *Kopp's Jahresb.* 1857, p. 357.
BOUIS AND PIMENTEL.   *Compt. rend.* 44, 1355; *J. pr. Chem.* 73, 176; *Kopp's Jahresb.* 1857, p. 356.

*Talgfett.   Stéarine* or *Substance grasse* of Chevreul.   *Suif absolu* of Braconnot. First prepared, though in an impure state, by Chevreul; purer by Braconnot. Berthelot's researches have demonstrated the identity of the stearin of natural fats with tristearin.

*Occurrence.*   In many fats, especially in the solid tallows and lards of the animal kingdom (xvi, 385—400). The *stearophanin* of Francis is also resolved by saponification into stearic acid and glycerin, but differs widely from tristearin in its melting point (p. 366).

*Preparation.*   Monostearin is heated for three hours with 15 to 20 times its weight of stearic acid to 270° in a sealed tube, and the product is purified in the same manner as monostearin (Berthelot); Heintz (*Ann. Pharm.* 92, 300) heats stearic acid with glycerin to 200° for 24 hours in a sealed tube filled with carbonic acid gas; the tube is

then opened; the glycerin decanted; the free stearic acid removed by treatment with ether and lime; and the mass of glycerides dissolved out by boiling ether. The mixture thus obtained already contains monostearin, and may be converted into tristearin by heating to 270° for eight hours with a large excess of stearic acid; the uncombined stearic acid may then be removed as before, and the tristearin dissolved out by hot ether.

Chevreul's stearin is obtained by dissolving mutton-suet in boiling alcohol, and recrystallising the fat which separates out, till the melting point becomes constant. Purer than this is Braconnot's stearin, obtained by repeatedly melting mutton-suet with oil of turpentine; still purer is that of Lecanu, who melts mutton-suet in the water-bath, adds an equal quantity of ether, stirring all the while; presses the fat when cold, and re-crystallises it till the melting point rises to 62°. Above this temperature the melting point does not appear to be raised by repeated crystallisation from small quantities of ether; but it may still be raised by repeated crystallisation from 10 to 100 times its volume of ether. After 32 crystallisations thus performed, the melting point rises to 69·7° (Duffy); but the fat thus treated is still a mixture of tristearin and tri-palmitin (Heintz), as shown by its melting point, and by that of the acids (= 66·5°), separated from it by saponification. The melting points of the fatty acids obtained by saponifying different varieties of stearin, are as follows:—

| Chevreul's stearin | solidifying at | 44° | yields fatty acids melting at | 53° |
|---|---|---|---|---|
| Braconnot's | ,, ,, | 61° | ,, ,, | 62·3° |
| Lecanu's | ,, ,, | 62° | ,, ,, | 66° |
| Liebig & Pelouze's ,, | ,, | 60—62° | ,, ,, | 64—65° |
| Heintz's | ,, ,, | 62° | ,, ,, | 64° |

A stearin prepared by Redtenbacher, according to Lecanu's method, still contained olein, inasmuch as it yielded sebacic acid by dry distillation, and an acid melting at 65° by saponification. — From Brindonia tallow, according to Bouis and Pimentel, pure tristearin may be separated by recrystallisation, yielding by saponification an acid having the melting point of stearic acid.

*Properties.* White, pearly, shining nodules, with very fine needles (Bouis & Pimentel). Small pearly laminæ, resembling spermaceti or stearic acid (Lecanu). — Inodorous; tasteless; neutral. Volatile without decomposition in a vacuum (Chevreul). A non-conductor of electricity (Rousseau, *J. Pharm.* 9, 587).

The stearin of the natural fats, as well as that artificially prepared, exhibits two (or three) different melting points, since when heated it first becomes fluid and transparent, afterwards, when further heated, again solid and opaque, and lastly, a second time fluid (Heintz, Duffy, Kopp). It expands when heated, but on first melting undergoes a contraction of about $2\frac{1}{4}$ per cent.; near its second melting point it again expands, and at the moment of melting increases about 5 p. c. in volume (Kopp). — The first melting point of tristearin is 55°, the second 71·6°. Tallow-stearin melts first at 51—52°, and the second time at 62°; at 58° it is quite opaque (Heintz). With purer or less pure tallow-stearin, somewhat different temperatures are observed.

This phenomenon is not produced by the splitting up of tristearin into distearin and free acid, inasmuch as alcohol of 56° takes up no

stearic acid therefrom (Heintz). According to Duffy, it is to be explained by the hypothesis of three modifications of stearin.

a. *First modification.* Produced when stearin melting at 69·7° is heated to 73·7° or higher, and then cooled, when it solidifies only at 51·7°. It is solid below 52°, but melts at that temperature, passing into the second modification. Shining nodules of sp. gr. 0·9867 at 15°, 0·9600 at 51·5° (Duffy), 0·987 at 10° (H. Kopp).

b. *Second modification.* Produced by heating stearin of the first modification to 52° or a few degrees higher for some time, until the fused mass has again become solid. Lamellar, melting at 64·2°. Sp. gr. 1·0101 at 15° (Duffy).

c. *Third modification.* Forms the crystals of stearin which separate from ether. It is also formed when stearin is heated to 65° or 66°, after which it solidifies slowly at 62—63° to an opaque, friable, highly crystalline mass, and melts again only at 69·7°. Sp. gr. at 15° = 1·0179 ; at 51·5° = 1·009 ; at 65·5° = 0·9931 ; at 68·2° = 0·9746 (Duffy).

The sp. gr. of melted stearin at 65·5° is 0·9245 (Duffy). — Duffy's second modification is not obtained from pure stearin, which, however, contains the first and third modifications, even after several recrystallisations ; it is, therefore, not to be regarded as pure stearin (Heintz). — Tallow-stearin, melting at 60°, possesses at 50°, in the first modification, a volume = 1·031, and after passing into the second modification a volume = 1·008, the volume at 0° being = 1 ; its volume increases to 1·076 at the melting-point, and on melting to 1·127 (H. Kopp).

Melted stearin solidifies on cooling to a very indistinctly crystalline mass (Heintz), to a blistered mass, which exhibits transparent and dead-white portions (Bouis & Pimentel). The temperature of melted stearin falls several degrees below the solidifying point before the mass becomes solid, but rises again during solidification to 44° (Chevreul), 54° (Lecanu); it forms a semi-transparent mass, having an even surface, the central point of which ultimately solidifies in radiated crystals (Chevreul).

| | | Chevreul. | Lecanu. | Liebig & Pelouze. |
|---|---|---|---|---|
| 114 C | 684 | 76·85 | 77·7 | 76·91 .... 74·52 to 76·09 |
| 110 H | 110 | 12·36 | 11·8 | 12·39 .... 12·39 „ 12·32 |
| 12 O | 96 | 10·79 | 10·5 | 10·70 |

| $C^6H^5O^3,3C^{36}H^{35}O^3$ | 890 | 100·00 | 100·0 | 100·00 |

| | Arzbächer. | Duffy. | | | Heintz. | | Berthelot. |
|---|---|---|---|---|---|---|---|
| | | a. | b. | c. | a. | b. | |
| C | 76·51 | 77·12 | 76·32 | 76·87 | 76·74 | 76·50 | 75·8 |
| H | 12·28 | 12·30 | 12·32 | 12·20 | 12·42 | 12·41 | 12·4 |
| O | 11·21 | 10·58 | 11·36 | 10·93 | 10·84 | 11·09 | 11·8 |

| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·0 |

Berthelot analysed artificially prepared tristearin. The stearin of beef-suet contains, according to Arzbächer, 78·74 p. c. C ; but Heintz (b) and Duffy (c) found it to have the same composition as that from mutton suet. Duffy examined stearin melting (a) at 62·5° and (b) at 69·7°. The formula of tristearin was deduced by Berthelot from the combining proportions of glycerin with acids (ix, 491 ; xvi, 351), Duffy

having previously shown that in the formation of 1 at. of stearic acid from stearin 2 at. of carbon are eliminated. Berthelot's formula alone (none of those previously proposed for tallow-fat, vii. 235) explains how, in the saponification of stearin, the under-mentioned amounts of glycerin and acid can be produced.

*Decompositions.* 1. Stearin when submitted to *dry distillation* boils without becoming much coloured, partly volatilising unaltered, and being partly decomposed, with formation of carbonic acid, gaseous and liquid hydrocarbons, acrolein (ix, 365), acetic acid, stearic acid, water, and carbon, which remains behind. Chevreul found also sebacic acid, though only in the case of stearin containing olein. The hydrocarbons boil between 190° and 245°, and are polymeric with olefiant gas (Gerhardt, *Rev. scient.* 19, 11). Bussy and Lecanu obtained from tallow-fat the same products as from drying fat (xvi, 308), but with a much larger proportion of solid fatty acids; even on rapid distillation, the distillate solidified, almost up to the end of the process. See also Dupuy (*J. Chim. méd.* 1, 378; *Ann. Chim. Phys.* 29, 319), and Lecanu (*J. Chim. méd.* 1, 458). — 2. Pure stearin does not undergo alteration in the *air,* and in an impure state probably turns rancid only when it contains olein or drying fat, and less quickly than those substances (Chevreul). Hog's lard spread upon the sides of a vessel filled with oxygen, and left to stand for three years, without exposure to sunlight, absorbs the greater part of the oxygen, and does not form carbonic acid, or only a very small quantity. It appears white, smells rancid and sour, and gives up to water caproic or similar acids, oleic acid, a non-volatile acid soluble in water, and yellow colouring matter. The portion insoluble in water contains free oleic acid, margaric, and stearic acids, yellow colouring matter, and unchanged fats (Chevreul, *Recherches,* 453). — 3. Stearin *burns* with a more luminous flame than drying- or oil-fat. — 4. It is not altered by digestion with 100 parts of *nitric acid* of sp. gr. 1·28 in the cold; when boiled therewith for an hour it evolves a little nitric oxide. By repeatedly distilling and pouring back the distillate till the residue dissolves therein, and afterwards evaporating the solution, succinic acid and a yellow acid oil having a bitter and harsh taste, are obtained (Chevreul). — 5. *Bromine* and *chlorine* readily act upon stearin, forming products more fusible than stearin, heavier than water, and having, according to Lefort, the formulæ $C^{76}Cl^4H^{66}O^8$ and $C^{76}Br^4H^{66}O^8$ (Lefort, *Compt. rend.* 37, 28). *Iodine* does not act upon stearin (Lefort). — 6. *Hydrochloric acid* produces from beef-suet oleic acid and a little stearic acid, leaving the rest unaltered (Braconnot). — 7. When melted stearin is mixed with half its weight of *oil of vitriol,* and the reddish compound formed is immediately washed with a large quantity of boiling water, stearic acid and oleic acid are produced (Braconnot). Stearin with 10 parts of oil of vitriol becomes immediately yellow, and after 24 hours, of a darker colour, which it imparts to the oil of vitriol; it softens and evolves sulphurous acid, and when heated to 100° after standing for eight days, it dissolves to a roseate, transparent, thickish liquid, with liberation of sulphurous acid. Above 100° it carbonises and froths up, from evolution of sulphurous acid (Chevreul). A mixture of hog's lard and an equal quantity of oil of vitriol, heated to 100° for a few minutes, and diluted with water after eight days, yields glycerin-sulphuric or sulphoglyceric acid (ix, 491) (Chevreul). Stearin behaves towards oil of vitriol and sugar-water in the same manner as stearic acid (Benecke).

8. By the *saponification* of stearin, which is effected with greater difficulty than that of olein (p. 87), 95·5 p. c. of stearic acid and 10·22 p. c. of glycerin are produced (Heintz),

$$C^{114}H^{110}O^{12} + 6HO = C^6H^8O^6 + 3C^{36}H^{36}O^4;$$
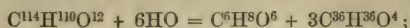
(by calculation 10·34 p. c. glycerin, and 95·73 p. c. stearic acid).   (See vii, 235). Duffy obtained from tallow-stearin, 95·59 to 95·76 p. c. (Bouis & Pimentel); from Brindonia-stearin, 95·72 p. c. of stearic acid. — Stearin resists the action of hydrate of lime at 100° for some minutes (Berthelot).   When heated in a water-bath for four hours with oxide of lead and absolute alcohol it does not form lead-plaster (Duffy).   Stearin, saponified with small quantities of aqueous alkali, yields neither mono-stearin nor distearin on decomposition (Bouis). — If alcoholic potash be added to an ethereal solution of stearin till a precipitate is produced, and the liquid be heated, the precipitate disappears.   The solution then contains stearic ether and stearate of potash, and is decomposed by acids, a mixture of stearic ether, stearic acid, and tristearin being precipitated.   The ether is always formed when the alcoholic potash employed is not sufficient to take up the whole of the stearic acid, and the mixture is allowed to react for a minute or two (Bouis). — 9. Stearin is apparently not altered by boiling with alcoholic ammonia (Duffy). — 10. It forms stearate of ethyl when boiled with absolute *alcohol* and 3 at., but not with 6 at., of *sodium*.   With fusel-oil it yields stearate of amyl (Duffy). — 11. Stearin is not decomposed by heating to 100° for 106 hours with alcoholic *acetic acid* (Berthelot). — 12. Mixed with *pancreatic juice*, it yields an emulsion, in which the whole of the stearin is converted into acid and glycerin on standing for a day or two at a temperature of 30° or 40° (Bernard, Berthelot).

Stearin is not perceptibly soluble in *alcohol* of 36° B., nor even in alcohol of 97 p.c., in the cold; it dissolves abundantly in hot alcohol, and separates in flocks on cooling (Lecanu).   100 parts of boiling alcohol of sp. gr. 0·795 dissolve 15·04 to 16·07 parts of Chevreul's tallow-fat from mutton suet; 15·48 parts of that from beef suet; 18·25 from hog's lard; and 36 from goose-fat.   100 parts of boiling alcohol of sp. gr. 0·805 dissolve 6·63 parts of tallow-fat; 100 parts of sp. gr. 0·822 dissolve 1·45 of the tallow-fat of butter, which is deposited almost entirely on cooling (Chevreul).   Stearin precipitated from an alcoholic solution retains alcohol even after prolonged fusion (Saussure).

Stearin dissolves very freely in boiling *ether* which retains $\frac{1}{2\frac{1}{2}5}$th on cooling (Lecanu).   It dissolves in hot *acetone* more freely than in cold, and is precipitated on cooling, or by the addition of water (Chenevix). — It is easily soluble in *volatile oils*, and mixes with melted *camphor* and with *drying* and *oil-fat*. — A solution of 1 part of stearin in 160 parts of almond oil deposits white flocks of stearin when mixed with 170 parts of ether; it is therefore not rendered more soluble in ether by admixture with a fatty oil (Lecanu).

## Stearochlorhydrin.

$$C^{42}H^{41}ClO^6 = C^6H^6ClO^3,C^{36}H^{35}O^3.$$

BERTHELOT.   *N. Ann. Chim. Phys.* 41, 304.
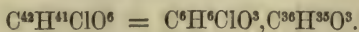
When a mixture of stearic acid and glycerin, heated to 100°, is saturated with hydrochloric acid gas, maintained at that temperature for some hours, and afterwards left to stand for several days or weeks at ordinary temperatures, a compound of the two acids with glycerin is formed, with elimination of water:

$$C^{36}H^{35}O^4 + C^6H^8O^6 + HCl = C^{42}H^{41}ClO^6 + 4HO.$$
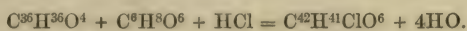
On neutralising with soda, the new body separates in the form of an oily layer. It is crystallisable, and after repeated solution in ether melts at 28°.

|  |  |  |  |  | Berthelot. |
|---|---|---|---|---|---|
| 42 C | ......................... | 252·0 | ........ | 66·93 | ........ | 65·0 |
| 41 H | ......................... | 41·0 | ........ | 10·89 | ........ | 11·9 |
| Cl | ......................... | 35·5 | ........ | 9·43 | ........ | 11·1 |
| 6 O | ......................... | 48·0 | ........ | 12·75 | ........ | 12·0 |
| $C^6H^6ClO^3,C^{36}H^{35}O^3$, | .... | 376·5 | ........ | 100·00 | ........ | 100·0 |

## Stearate of Amyl.

$$C^{46}H^{46}O^4 = C^{10}H^{11}O,C^{36}H^{35}O^3.$$
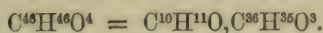
DUFFY. *Chem Soc. Qu. J.* 5, 197; *J. pr. Chem.* 58, 363.
HANHART. *Compt. rend.* 47, 230; *J. pr. Chem.* 77, 5; *Kopp's Jahresb.* 1858, p. 301.

*Stearinmylester.*

Obtained by heating stearic acid with amyl-alcohol to 200° in a sealed tube for a day. The uncombined acid is removed as in the preparation of palmitin (xvi. 353), and the uncombined amyl-alcohol by treatment with alcohol, which dissolves only a little of the ether (Hanhart). — Stearate of amyl is also formed by boiling tristearin with a solution of sodium in amyl-alcohol (Duffy).

Neutral, transparent, soft, and viscous mass, melting at 25·5° (Duffy), 25° (Hanhart). — It is decomposed by alcoholic, but not by aqueous potash. Dissolves (slightly according to Hanhart) in alcohol, the solution solidifying to a jelly. The ethereal solution also does not yield crystals (Duffy).

## Benzostearic Anhydride.

$$C^{50}H^{40}O^6 = C^{14}H^5O^3,C^{36}H^{35}O^3.$$
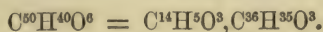
CHIOZZA. *Ann. Pharm.* 91, 104; *J. pr. Chem.* 64, 33; *Pharm. Centr.* 1854, 794.

*Benzoyl-stearat.*

A mixture of stearate of potash and chloride of benzoyl is heated in a water-bath till the smell of the latter disappears, and the product is extracted with ether.

Shining laminæ, melting at 70°.

|  |  |  |  |  |  |  | Chiozza. |
|---|---|---|---|---|---|---|---|
| 50 C | ........................ | 300 | ........ | 77·32 | ........ | 77·1 |
| 40 H | ........................ | 40 | ........ | 10·31 | ........ | 10·3 |
| 6 O | ........................ | 48 | ........ | 12·37 | ........ | · 12·6 |
| $C^{14}H^5O^3,C^{36}H^{35}O^3$ | ........ | 388 | ........ | 100·00 | ........ | 100·0 |

Chiozza gives for this compound the formula of benzomargaric anhydride, but designates it by the above name.


## Stearate of Orcin.

$$C^{50}H^{42}O^6 = C^{14}H^7O^3,C^{36}H^{35}O^3.$$
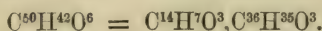
BERTHELOT.   *N. Ann. Chim. Phys.* 56, 74 ; *Lieb. Kopp. Jahresber.* 1855, 677.

*Orcine stéarique.*

When orcin (xiv. 353) is heated with stearic acid to 200° in a sealed tube for some hours, a mixture is obtained from which water extracts the uncombined orcin. On separating the excess of stearic acid from the residue by means of ether and hydrate of lime, according to xv. 353, the stearate of orcin remains dissolved in the ether, and is purified by evaporation and solution in bisulphide of carbon.

Slightly coloured, tasteless, neutral wax, which, when heated, evolves an odour of orcin and stearic acid, and volatilises. — Combustible. Assumes a red colour with ammonia. — Heated to 100° for some days with moist hydrate of lime, it yields stearate of lime and a substance soluble in water and alcohol; the latter body becomes coloured with ammonia, like orcin, but does not form crystals.

Stearate of orcin is insoluble in *water*, but easily soluble in *ether* and *bisulphide of carbon.*


## Stearate of Capryl.

$$C^{52}H^{52}O^4 = C^{16}H^{17}O,C^{36}H^{35}O^3.$$
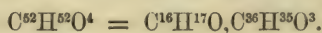
HANHART.   *Compt. rend.* 47, 230 ; *J. pr. Chem.* 77, 5.

*Stearincaprylester.*

Obtained from stearic acid and capryl-alcohol in the same manner as stearate of amyl. — Melts at − 4·5°. Colourless, inodorous, tasteless, and neutral.


## Stearate of Opianyl.

$$C^{92}H^{78}O^{12} = C^{20}H^8O^6,2C^{36}H^{35}O^3.$$
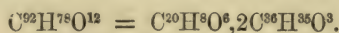
BERTHELOT.   *N. Ann. Chim. Phys.* 56, 75.

*Meconine stéarique.*

Formed by heating opianyl (meconin) with stearic acid to 200° for

several hours; boiling the product with water, which takes up uncombined opianyl; and removing the excess of stearic acid by means of lime and ether, as with palmitin (xvi. 353).

Neutral, white, solid mass, which melts easily and solidifies very slowly.

|  |  |  |  |  | Berthelot. |
|---|---|---|---|---|---|
| 92 C | ................................ | 552 | ........ | 76·03 | ........ | 75·3 |
| 78 H | ................................ | 78 | ........ | 10·74 | ........ | 11·2 |
| 12 O | ................................ | 96 | ........ | 13·23 | ........ | 13·5 |
| $C^{20}H^8O^6,2C^{36}H^{35}O^3$ | ...... | 726 | ........ | 100·00 | ........ | 100·0 |

## Stearate of Camphyl.

$$C^{56}H^{52}O^4 = C^{20}H^{17}O,C^{36}H^{35}O^3.$$
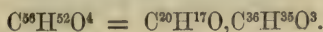
BERTHELOT. *N. Ann. Chim. Phys.* 56, 89; *Chimie organ.* 1, 151.

*Camphol stéarique. Stearinsaures Borneol. Stearinbornester.*

Obtained by heating stearic acid with borneol (xiv. 332) to 200° for eight or ten hours in a sealed tube; water is then eliminated and a mass is formed from which the uncombined stearic acid is removed by cautious and rapid treatment with ether and hydrate of lime, and the free borneol by heating the evaporated ethereal solution to 150° in an air-bath for half a day or longer.

Thick, colourless and inodorous oil, which solidifies to a crystalline mass after some days or months. Neutral when freshly prepared. Volatile (without decomposition?). Decomposed by alkalis into stearic acid and borneol. — Dissolves slightly in cold, and easily in boiling *alcohol* and in *ether*.

|  |  |  |  |  | Berthelot. *mean.* |
|---|---|---|---|---|---|
| 56 C | ................................ | 336 | ........ | 80·00 | ........ | 79·8 |
| 52 H | ................................ | 52 | ........ | 12·38 | ........ | 12·5 |
| 4 O | ................................ | 32 | ........ | 7·62 | ........ | 7·7 |
| $C^{20}H^{17}O,C^{36}H^{35}O^3$ | ........ | 420 | ........ | 100·00 | ........ | 100·0 |

## Bistearate of Pinityl.

$$C^{84}H^{80}O^{14} = C^{12}H^{10}O^8,2C^{36}H^{35}O^3.$$
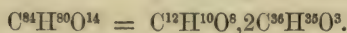
BERTHELOT. *Compt. rend.* 41, 454; *Chim. organ.* 216; *Lieb. Kopp. Jahresber.* 1855, 677.

*Pinite monostéarique. Bistearinpinitester.*

Pinite is heated with stearic acid to 200—250° in a sealed tube for some hours, and the product is purified as in the case of palmitin (xvi, 353).

Solid, white, neutral mass, resembling stearin. When decomposed with hydrate of lime, it yields 21 p. c. of pinite (calc. 23 p. c. $C^{12}H^{12}O^{10}$).

## Quadristearate of Pinityl.

$$C^{156}H^{152}O^{22} = C^{12}H^{12}O^{10},4C^{36}H^{35}O^3.$$
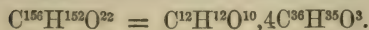
BERTHELOT.   *Chim. organ.* 2, 216.

*Pinite distéarique.   Quadristearinpinitester.*

Obtained by heating bistearate of pinityl with stearic acid to 220°.
Solid waxy mass, possessing externally all the characters of stearin.
Neutral.

## Bistearate of Quercityl.

$$C^{84}H^{80}O^{14} = C^{12}H^{10}O^8,2C^{36}H^{35}O^3.$$
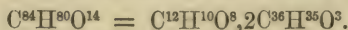
BERTHELOT.   *Chim. organ.* 2, 219.

*Quercite stéarique.   Bistearinquercitester.*

Obtained by heating quercite with stearic acid to 200° for some
hours in a sealed tube. — Solid white mass, resembling stearin. —
Soluble in ether, but insoluble in water. — Yields quercite and stearic
acid by decomposition with hydrate of baryta.

## Bistearoglucose.

$$C^{84}H^{78}O^{14} = C^{12}H^8O^6,2C^{36}H^{35}O^3.$$
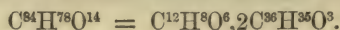
BERTHELOT.   *N. Ann. Chim. Phys.* 60, 95; *Chim. organ.* 2, 289.

*Glucose stéarique.* — A monosaccharide of the 2nd class.   See xv, 318.

A mixture of stearin and anhydrous glucose is heated to 120° for
fifty or sixty hours, and the product is purified according to xvi, 353.
Cane-sugar and trehalose (xv, 299) also yield the same compound;
when trehalose is employed the mixture may be heated to 180°. Small
quantities are obtained likewise from stearin and starch at 180°, and
from stearin and woody fibre at 200°.

Microscopic, fine granules, or white fusible mass resembling stearin.
Neutral.

|  |  |  |  |  |  | Berthelot. |
|---|---|---|---|---|---|---|
| 84 C | ............................. | 504 | ........ | 72·62 | ........ | 72·4 |
| 78 H | ............................. | 78 | ........ | 11·24 | ........ | 11·0 |
| 14 O | ............................. | 112 | ... .... | 16·14 | ........ | 16·6 |
| $C^{12}H^8O^6,2C^{36}H^{35}O^3$ | ........ | 694 | ........ | 100·00 | ........ | 100·0 |

Assumes with *oil of vitriol* a reddish colour, quickly changing to
violet and black. — Reduces *potassio-cupric tartrate.* — Decomposed by
treatment with warm alcoholic *hydrochloric acid*, with formation of
glucose, humus-substances, and stearate of ethyl.

Bistearoglucose is insoluble in water, but forms an emulsion when shaken therewith. It dissolves in *absolute alcohol* and in *ether*.

## Quadristearate of Mannityl.

$$C^{156}H^{152}O^{22} = C^{12}H^{12}O^{10},4C^{36}H^{35}O^3.$$
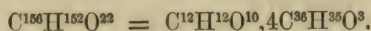
BERTHELOT. *N. Ann. Chim. Phys.* 47, 324; *Chim. organ.* 2, 191; *Lieb. Kopp. Jahresber.* 1856, 659.

*Mannite distéarique.* — *Quadristearinmanitanester* (see xvi, 362).

Mannite, or mannitan, is heated with stearic acid to 200° or 250° for 15 or 20 hours, and the product is purified according to xvi, 353.

Microscopic, white crystals, or solid, white, fusible mass, resembling stearin. Neutral.

Heated on platinum foil it gives off vapours, having at last an odour of caramel, then carbonises and burns.

Decomposed by baryta and oxide of lead at 100°, and in a few hours by water at 240°. — It is not altered by heating for 8 or 10 hours with mannite. In the decomposition with baryta 13·2 p. c. of mannitan is obtained (by calc. 13 p. c. $C^{12}H^{12}O^{10}$).

|  |  |  |  |  | Berthelot. mean. |
|---|---|---|---|---|---|
| 156 C ...................................... | 936 | ........ | 74·05 | ........ | 73·93 |
| 152 H ................................. | 152 | ........ | 12·03 | ........ | 12·03 |
| 22 O...................................... | 176 | ........ | 13·92 | ........ | 14·04 |
| $C^{12}H^{12}O^{10},4C^{36}H^{35}O^3$ ........ | 1264 | ........ | 100·00 | ........ | 100·00 |

## Sexstearate of Mannityl.

$$C^{228}H^{216}O^{22} = C^{12}H^{6}O^{4},6C^{36}H^{35}O^3.$$
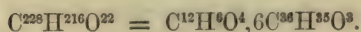
BERTHELOT. *N. Ann. Chim. Phys.* 47, 324; *Chim. organ.* 2, 192; *Lieb. Kopp. Jahresber.* 1856, 659.

*Mannite tristéarique.* *Hexastearinmannitanester* (xv, 362).

Quadristearate of mannityl is heated with a large excess of stearic acid to 200 — 250° for 20 or 30 hours, and the neutral mass thus obtained is separated, and again treated in the same way with an excess of stearic acid. — Neutral mass, resembling tristearin (p. 119).

|  |  |  |  |  | Berthelot. |
|---|---|---|---|---|---|
| 228 C ........................... | 1368 | ........ | 77·73 | ........ | 77·9 |
| 216 H ........................... | 216 | ........ | 12·27 | ........ | 12·6 |
| 22 O ........................... | 176 | ........ | 10·00 | ........ | 9·5 |
| $C^{12}H^{6}O^{4},6C^{36}H^{35}O^3$ .... | 1760 | ........ | 100·00 | ........ | 100·0 |

## Bistearate of Dulcityl.

$$C^{84}H^{80}O^{14} = C^{12}H^{10}O^8, 2C^{36}H^{35}O^3.$$
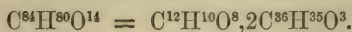
BERTHELOT.    *Compt. rend.* 41, 454; *Chim. organ.* 2, 210; *Lieb. Kopp. Jahresber.* 1855, 676.

*Dulcite monostéarique.    Bistearindulcitanester* (see xv, 386).

Obtained by heating stearic acid with dulcite to 200°, and purifying the product according to xvi, 353.

White, solid, crystallisable mass, resembling stearin. — Very slowly decomposed by hydrate of lime at 100°, yielding 25·4 p. c. of dulcitan, with an admixture of dulcite (calc. 23·6 p. c. $C^{12}H^{12}O^{10}$).

## Quadristearate of Dulcityl.

$$C^{156}H^{148}O^{18} = C^{12}H^8O^6, 4C^{36}H^{35}O^3.$$
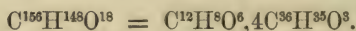
BERTHELOT.    *Compt. rend.* 41, 454; *Chim. organ.* 2, 211; *Kopp's Jahresber.* 1858, 677.

*Dulcite distéarique.    See xvi, 386.*

Obtained as a neutral mass by heating dulcite to 200° with a large excess of stearic acid. It is purified in the same manner as palmitin (xvi, 353), which it resembles.

## Stearate of Cetyl.

$$C^{68}H^{68}O^4 = C^{32}H^{33}O, C^{36}H^{35}O^3.$$
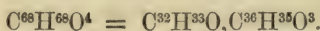
BERTHELOT.    *N. Ann. Chim. Phys.* 56, 70.

*Ethal stéarique.*

A mixture of 1 part of ethal with 4 or 5 parts of stearic acid is heated to 200° in a sealed tube, for 8 or 10 hours. The product is mixed first with a little ether and then with hydrate of lime, which takes up the uncombined stearic acid, and the whole is heated to 100° for some minutes, and afterwards boiled with ether, when the ethal and stearate of cetyl are dissolved, and remain behind on evaporating the solution. From the mixture thus obtained, the free ethal is removed by boiling five or six times with 6 to 10 parts of alcohol, and the undissolved cetyl-compound is then allowed to crystallise from ether.

Broad shining laminæ, resembling spermaceti, melting at 55° to 60°, and cooling to a crystalline solid. Volatilises with formation of a little free acid. Neutral.

|  |  |  |  |  |  | Berthelot. |
|---|---|---|---|---|---|---|
| 68 C | .................... | 408 | ........ | 80·31 | ........ | 80·0 |
| 68 H | .................... | 68 | ........ | 13·38 | ........ | 13·6 |
| 4 O | .................... | 32 | ........ | 6·31 | ........ | 6·4 |
| $C^{32}H^{33}O, C^{36}H^{35}O^3$ | .... | 508 | ........ | 100·00 | ........ | 100·0 |

Stearate of cetyl *burns* on platinum foil with a white flame. — It is decomposed by hydrate of lime, at 100°, only after 8 or 10 days.

Nearly insoluble in boiling *alcohol*. Dissolves slightly in cold, and freely in boiling *ether*.

## Stearone.

$$C^{70}H^{70}O^2 = C^{36}H^{36}O^2, C^{34}H^{34}.$$
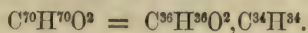
BUSSY. *Ann. Chim. Phys.* 53, 410; *J. Pharm.* 19, 642; *Ann. Pharm.* 9, 269; *J. pr. Chem.* 1, 179.
REDTENBACHER. *Ann. Pharm.* 35, 57.
VARRENTRAPP. *Ann. Pharm.* 35, 80.
ROWNEY. *Chem. Soc. Qu. J.* 6, 97; abstr. *Ann. Pharm.* 88, 285; *J. pr. Chem.* 59, 493; *N. Ann. Chim. Phys.* 39, 490.
HEINTZ. *Pogg.* 94, 272; 96, 65.

*Margarone. Stearene.* Discovered by Bussy.

Bussy distinguished stearone and *margarone*, the former from stearic acid, the latter from margaric acid, melting at 56°, obtained by the distillation of hog's lard. His margarone may, therefore, be regarded as a mixture of stearone and palmitone (xvi, 382). Redtenbacher, supposing that stearic acid is converted by distillation into margaric acid, described as margarone, stearone obtained from distilled, from commercial, and from pure stearic acid, and considered the existence of stearone as impossible. Varrentrapp's margarone was obtained from a mixture of fatty acids melting at 55—56° (Varrentrapp's margaric acid, xvi, 351), and is doubtless, like Bussy's, to be regarded as a mixture of palmitone and stearone.

*Formation.* By the dry distillation of stearic acid in the free state, or more abundantly, in combination with lime or oxide of lead.

*Preparation.*—1. Stearate of lime, or a mixture of melted stearic acid and hydrate of lime, is subjected to dry distillation, and the solid distillate is boiled for some time with water. The residue is finely powdered, heated with ether to boiling, and after cooling, collected on a filter and again treated with ether, when pure stearone remains undissolved (Heintz). Bussy purifies it by re-crystallisation from hot alcohol. — 2. Stearate of lead is distilled in a current of super-heated steam, and the nearly colourless distillate is purified as in the first method (H. L. Buff).

*Properties.* Delicate, pearly, microscopic laminæ, very strongly electric. Melting-point 87·8° (Heintz), 86° (Bussy), 82° from pure, 77° from commercial or distilled stearic acid (Redtenbacher), 76° (Varrentrapp; Rowney). Solidifies at 72° (Rowney). Bussy's margarone distils partially undecomposed.

|  |  |  |  |  | | Bussy. | |
|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | *a.* | *b.* |
| 70 C | 420 | ........ | 83·00 | ........ | 83·22 | ........ | 81·81 |
| 70 H | 70 | ........ | 13·84 | ........ | 13·77 | ........ | 13·50 |
| 2 O | 16 | ........ | 3·16 | ........ | 3·01 | ........ | 4·69 |
| $C^{70}H^{70}O^2$ | 506 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

|   | Redtenbacher. |   | Varrentrapp. |   | Rowney. |   | Heintz. $a$. |   | $b$. |
|---|---|---|---|---|---|---|---|---|---|
| C ........ | 82·59 | ........ | 81·18 | ........ | 82·12 | ........ | 82·98 | ........ | 82·91 |
| H ........ | 13·81 | ........ | 13·79 | ........ | 13·74 | ........ | 13·91 | ........ | 13·92 |
| O ........ | 3·60 | ........ | 5·03 | ........ | 4·14 | ........ | 3·11 | ........ | 3·17 |
|   | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

$a$ is Bussy's stearone, $b$ his margarone. Heintz analysed stearone from stearic acid ($a$), and from stearate of lime ($b$). The formulæ proposed for stearone have varied with that of stearic acid. Rowney gave the formula C$^{28}$H$^{28}$O; Heintz, the one above given.

*Decompositions.* 1. Margarone *burns* with a bright smokeless flame (Bussy). — 2. Melted stearone is converted by *bromine* into bromostearone, with evolution of hydiobromic acid (Heintz). In other experiments, Heintz obtained, by the action of a great excess of bromine at high temperatures, only a little bromostearone, but a large quantity of an easily fusible product, readily soluble in ether. — Rowney obtained, by the action of bromine on his stearene (melting at 72°), tufts of feathery crystals, melting at 43—45°, and containing, on the average, 59·86 p. c. C., 9·76 H., and 27·93 Br., corresponding to the formula C$^{28}$BrH$^{27}$O. *Iodine* is without action on stearone (Rowney). — 3. *Chlorine* forms with margarone, at a gentle heat, a colourless, transparent, viscid liquid (Bussy). — 4. Stearone becomes coloured with *oil of vitriol*, and carbonises, with evolution of sulphurous acid (Bussy. Rowney). — 5. Stearone is not acted upon by hot *nitric acid*, but is decomposed by nitro-sulphuric acid, with formation of an acid volatile oil (Rowney). — 6. *Potassium* acts upon margarone, evolving a little combustible gas (Bussy). — 7. Margarone, distilled with *quick lime*, yields carbonate of lime and a distillate melting at 60° (Bussy). — 8. Margarone is not decomposed by a boiling strong solution of *caustic potash* (Bussy).

Stearone dissolves very slightly in boiling *alcohol*, and is deposited almost entirely on cooling (Heintz). Bussy's margarone, melting at 77°, dissolves in 50 parts of boiling alcohol of 36°. — Stearone is nearly insoluble in cold, and very difficultly soluble in boiling *ether* (Heintz). Margarone dissolves in 5 parts of boiling *ether*, *acetate of ethyl*, or *oil of turpentine* (Bussy).

## Bromostearone.

$$C^{70}Br^2H^{68}O^2 = C^{36}H^{36}O^2,C^{34}Br^2H^{32}?$$
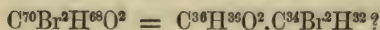
Heintz. *Pogg.* 96, 75.

When an excess of bromine is added to melted stearone, a red oil separates, which solidifies when shaken with water. This is to be washed, first with water containing ammonia, and afterwards with cold alcohol and re-crystallised from ether till the melting-point rises to 72°. It dissolves with moderate facility in cold ether.

| | _Laminæ._ | | | | Heintz. |
|---|---|---|---|---|---|
| 70 C | 420 | ........ | 63·26 | ........ | 63·03 |
| 2 Br | 160 | ........ | 24·09 | ........ | 24·38 |
| 68 H | 68 | ........ | 10·24 | ........ | 10·35 |
| 2 O | 16 | ........ | 2·41 | ........ | 2·24 |
| $C^{70}Br^2H^{68}O^2$ | 664 | ........ | 100·00 | ........ | 100·00 |

# Stearic Anhydride.

$$C^{72}H^{70}O^6 = C^{36}H^{35}O^3, C^{36}H^{35}O^3.$$
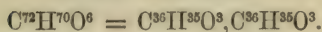
CHIOZZA. _Ann. Pharm._ 91, 104; _J. pr. Chem._ 64, 33; _Pharm. Centr._ 1854, 794.

_Anhydrous stearic acid._  _Wasserfreie Stearinsäure._

Obtained in the same manner as benzoic anhydride, but difficult to free from adhering stearic acid.

| | | | | | Chiozza. |
|---|---|---|---|---|---|
| 72 C | 432 | ........ | 78·54 | ........ | 77·7 |
| 70 H | 70 | ........ | 12·72 | ........ | 12·5 |
| 6 O | 48 | ........ | 8·74 | ........ | 9·8 |
| $C^{72}H^{70}O^6$ | 550 | ........ | 100·00 | ........ | 100·0 |

Chiozza calls this body stearic anhydride, but assigns to it the formula of margaric anhydride, $C^{68}H^{66}O^6$.

_Oxygen-nucleus_  $C^{36}H^{34}O^2$.

# Ricinoleic Acid.

$$C^{36}H^{34}O^6 = C^{36}H^{34}O^2, O^4.$$
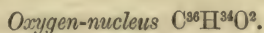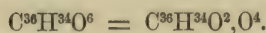
BUSSY & LECANU. _J. Pharm._ 13, 70; _Mag. Pharm._ 18, 47; _Berz. Jahrb._ 29, 1, 256.
SAALMÜLLER. _Ann. Pharm._ 64, 108.
SVANBERG & KOLMODIN. _J. pr. Chem._ 45, 431.
BOUIS. See xiii, 183. Complete: _N. Ann. Chim. Phys._ 44, 103, and 48, 99.
PETERSEN. _Ann. Pharm._ 118, 69.

_Sources._ In castor oil (see below). In the oil of _Jatropha Curcas_ (Bouis).

_Preparation._ Castor oil is saponified with potash or soda-ley, and the soap is salted out and decomposed by hydrochloric acid. The oily mixture of ricinoleic acid with a small quantity of solid fatty acids is then cooled to − 10° or − 12° with $\frac{1}{3}$rd its volume of alcohol, when the solid acids crystallise out, and are removed. After driving off the alcohol, the ricinoleic acid is digested with excess of oxide of lead, and the lead-salt formed is dissolved in ether, and decomposed with hydrochloric

acid and water. The ricinoleic acid, which is left on evaporating the ethereal layer, is purified by dissolving it in aqueous ammonia, precipitating with chloride of barium, and crystallising the baryta-salt from alcohol, as with oleic acid (p. 64). From the baryta-salt the acid is obtained by decomposition with aqueous hydrochloric acid (Saalmüller, Svanberg, and Kolmodin). In the decomposition of the baryta-salt the presence of alcohol is to be avoided, as its subsequent removal is attended with difficulty (Saalmüller).

*Properties.* Pale wine-yellow oil, colourless in thin layers, of the consistence of syrup. Sp. gr. 0·94 at 15°. Solidifies completely at − 6° to − 10°, to a granular mass. Inodorous. Has a very disgreeable, persistent, harsh taste. An alcoholic solution reddens litmus (Saalmüller).

|  | In vacuo over oil of vitriol. | | Saalmüller. mean. | Bouis. |
|---|---|---|---|---|
| 36 C ............ | 216 | ........ 72·48 | ........ 73·23 | ........ 71·99 |
| 34 H ............ | 34 | ........ 11·41 | ........ 11·59 | ........ 11·51 |
| 6 O ............ | 48 | ........ 16·11 | ........ 15·18 | ........ 16·50 |
| $C^{36}H^{34}O^6$ .... | 298 | ........ 100·00 | ........ 100·00 | ........ 100·00 |

Bouis' acid was prepared from the amide. — Saalmüller gives the formula $C^{38}H^{36}O^6$, which agrees with his analyses better than the above formula of Svanberg and Kolmodin. Later analyses, however, as well as the decomposition-products of the substance appear to support the formula with 36 at. C., which is now generally adopted.

*Decompositions.* 1. Ricinoleic acid, subjected to *distillation,* yields at first a limpid, and afterwards a thick and repulsive-smelling distillate, free from sebacic acid (Saalmüller). — 2. It does not absorb oxygen from the *air,* nor even on long exposure to the gas, and does not form carbonic acid (Saalmüller). The acid appears to undergo alteration in the air (Svanberg & Kolmodin). — 3. It absorbs a little sulphurous acid gas, without becoming solid or otherwise altered (Saalmüller). See also the decompositions of castor oil.

4. By the dry distillation of ricinoleates of the alkalis, various products are obtained, according as the neutral salt is distilled alone, or with an excess of alkali. (See xiii, 183, 187, 189, and xiv, 494.)
*a.* By cautiously distilling the *neutral soda-salt,* until the residue begins to froth up, a distillate of œnanthol (xii, 446) is obtained, the residue containing the soda-salt of the same acid that is formed by the dry distillation of castor-oil (see below). The soda-salt and the glyceride of ricinoleic acid are, therefore, decomposed in the same manner by distillation (Städeler). According to Bouis, the neutral ricinoleates of the alkalis yield, by dry distillation, caprylic aldehyde (xiii, 187), and a peculiar acid :

$$C^{36}H^{34}O^6 = C^{16}H^{16}O^2 + C^{20}H^{18}O^4 \text{ (Bouis).}$$
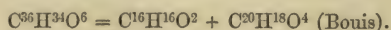
The residue froths up only when more strongly heated, and yields a brown fetid distillate, containing only a little œnanthol, and no other aldehyde (Städeler).
*b.* A mixture of ricinoleate of potash or soda, *with excess of hydrate of potash or soda,* froths up when heated, evolves an odour of mushrooms, and thickens ; at about 250° it ceases frothing, and gives off a

large quantity of hydrogen (no carbonic acid), and a volatile oil, leaving a light spongy residue, which is inflammable while hot. By further heating, this residue is also decomposed, with formation of white vapours having a repulsive odour (Bouis). A mixture of castor-oil and excess of hydrate of soda behaves in the same manner when heated.

From the *residues*, acids separate a white mass which gives up sebacic acid (xiv, 493) to hot water. The remainder consists of a dark, viscid oil (amounting to half the volume of the oil when castor-oil instead of ricinoleic acid is employed), which is saponifiable to a white, hard soap, deposits crystals of palmitic acid in the cold, and solidifies only partially with nitrous acid (Bouis). According to Bouis, sebacic acid is produced more especially by very rapid, and to a less extent by slow heating.

The volatile oil contains two constituents, one only of which combines with bisulphites of the alkalis in the manner of an aldehyde (Limpricht). According to Limpricht's earlier views, which were adopted by Bouis, this aldehyde-like body is to be regarded as caprylic aldehyde (xiii, 187); but according to the statements of Städeler, which were confirmed by Dachauer & Petersen, and are now accepted by Limpricht, it must be regarded as methyl-œnanthol (xiv, 189). — The second body, which does not combine with bisulphites of the alkalis, is, according to Bouis, Moschnin, Squire, Cahours, Limpricht, Malaguti, and Dachauer (*Ann. Pharm.* 106, 269), caprylic alcohol (xiii, 183); but, according to Railton, Wills, Städeler, and Petersen, it is œnanthylic alcohol; according to E. T. Chapman (*N. Chem. Soc. J.*, 3, 290), sometimes the one, sometimes the other alcohol is produced.

The alcohol is produced more especially, together with a salt of sebacic acid, by heating rapidly, so that the alkali fuses; the aldehyde, by heating slowly to 225° or 230°, in which case less sebacic acid is formed (Bouis). These statements are not in accordance with the results obtained by Malaguti and Limpricht (xiv, 494). — The decomposition may be represented by the following equations: *a.* when methyl-œnanthol or capryl-aldehyde is formed:

$$C^{36}H^{34}O^6 + 4HO = C^{16}H^{16}O^2 + C^{20}H^{18}O^8 + 4H.$$
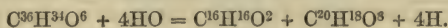
*b.* When caprylic alcohol is produced:

$$C^{36}H^{34}O^6 + 4HO = C^{16}H^{18}O^2 + C^{20}H^{18}O^8 + 2H.$$
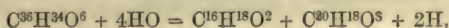
*c.* When œnanthylic alcohol is formed:

$$C^{36}H^{34}O^6 + 4HO = C^{14}H^{16}O^2 + C^{20}H^{18}O^8 + C^2H^4.$$
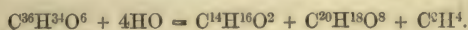
In this last reaction marsh-gas (or a secondary product) must be formed, unless the œnanthylic alcohol results from the further decomposition of the sebate (Städeler).

*Ricinoleates.* The alcoholic solution of the acid expels carbonic acid from alkaline carbonates. The salts are all soluble in alcohol, and some also in ether. They do not become oxidised on keeping (Saalmüller).

*Ricinoleate of Baryta.* — Preparation (p. 132). On treating with warm alcohol, a portion generally remains undissolved in the form of a tough yellow mass (Saalmüller). — White laminæ, very soft to the

touch, or crystalline crusts (Saalmüller).    Melts at 100°, without loss of weight, to a tenacious mass, which may be drawn out in threads like boracic acid, and becomes translucent and brittle on cooling (Bouis). Dissolves slightly in cold water, in 300 parts of cold alcohol of 95 p. c., and easily in hot alcohol, crystallising on cooling (Svanberg & Kolmodin).

| In vacuo, over oil of vitriol. | | | | | Saalmüller mean. | | Svanberg & Kolmodin. |
|---|---|---|---|---|---|---|---|
| 36 C ...................... | 216 | ........ | 59·10 | ........ | 59·81 | ........ | 58·69 |
| 33 H ..................... | 33 | ........ | 9·03 | ........ | 9·38 | ........ | 8·96 |
| 5 O ...................... | 40 | ........ | 10·94 | ........ | 10·54 | ........ | 11·57 |
| BaO ..................... | 76·5 | ........ | 20·93 | ........ | 20·27 | ........ | 20·78 |
| $C^{36}H^{33}BaO^6$ ........ | 365·5 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Bouis found 20·45, Petersen 20·99 p. c. baryta.

*Strontia-salt.*  Precipitated from the ammonia-salt by chloride of strontium.  Crystallises from alcohol in small white granules (Saalmüller).

| | | | | | Saalmüller. |
|---|---|---|---|---|---|
| $C^{36}H^{33}O^5$ ................ | 289 | ........ | 84·75 | | |
| SrO ................ | 52 | ........ | 15·25 | .... | 14·6 |
| $C^{36}H^{33}SrO^6$ ........ | 341 | ........ | 100·00 | | |

*Lime-salt.* — Obtained from the ammonia-salt by precipitation with chloride of calcium.  Crystallises from alcohol in small white scales, which lose water when melted, even after long drying in a vacuum over oil of vitriol.  Melts at 80° to a pale-yellow transparent mass, which is brittle and friable when cold (Saalmüller).

| | At 100° | | | | Saalmüller. mean. |
|---|---|---|---|---|---|
| 36 C........................... | 216 | ........ | 68·14 | ........ | 66·38 |
| 33 H .................... | 33 | ........ | 10·41 | ........ | 10·59 |
| 5 O........................ | 40 | ........ | 12·61 | ........ | 14·57 |
| CaO ................ | 28 | ........ | 8·84 | ........ | 8·46 |
| $C^{36}H^{33}CaO^6$ ........ | 317 | ........ | 100·00 | ........ | 100·00 |

Saalmüller supposes the salt to contain 1 at. of water, the presence of which has not, however, been demonstrated.

*Magnesia-salt.* — Very fine needles, insoluble in water but easily soluble in alcohol.  Contains, after drying over oil of vitriol, 5·69 p. c. MgO. (Saalmüller).

| | | | | | Petersen. |
|---|---|---|---|---|---|
| 36 C..................... | 216 | ........ | 69·90 | ........ | 70·08 |
| 33 H .... ............ | 33 | ........ | 10·68 | ........ | 10·53 |
| 5 O..................... | 40 | ........ | 12·95 | ........ | 13·34 |
| MgO..................... | 20 | ........ | 6·47 | ........ | 6·05 |
| $C^{36}H^{33}MgO^6$ .... | 309 | ........ | 100·00 | ........ | 100·00 |

*Zinc-salt.* — Crystallises from alcohol in small white granules (Saalmüller).

| | | | | |
|---|---|---|---|---|
| $C^{36}H^{33}O^5$ ............ | 289 | ........ | 87·79 | |
| ZnO ............ | 40·2 | ........ | 12·21 | ........ 11·85 |
| $C^{36}H^{33}ZnO^6$ .... | 329·2 | ........ | 100·00 | |

*Lead-salt.* — The acid, when heated with excess of lead-oxide, loses 2·9 to 3·6 p. c. of water (1 at. = 3·02 p. c.), and forms a solid compound, the ethereal solution of which, on evaporation over oil of vitriol, leaves the lead-salt as a transparent crystalline mass. — Melts at 100° to a light brown viscid liquid, and solidifies to an easily pulverisable mass. Dissolves very easily in ether (Saalmüller). Dissolves in cold, and not much more freely in hot alcohol (Svanberg & Kolmodin). — By precipitating ammoniacal ricinoleic acid with neutral acetate of lead, a curdy precipitate of variable composition is obtained (Saalmüller).

|  | *At 100°, over oil of vitriol.* |  |  |  | Saalmüller. *mean.* |
|---|---|---|---|---|---|
| 36 C | 216 | ............ | 53·87 | ............ | 54·58 |
| 33 H | 33 | ............ | 8·23 | ............ | 8·61 |
| 5 O | 40 | ............ | 9·97 | ............ | 9·69 |
| PbO | 112 | ............ | 27·93 | ............ | 27·12 |
| $C^{36}H^{33}PbO^6$ | .... | 401 | ............ | 100·00 | ............ 100·00 |

*Silver-salt.* — Nitrate of silver throws down from the ammonia-salt a curdy precipitate, which, when treated with alcohol or ether, partially dissolves, but for the most part blackens and remains undissolved (Saalmüller). It softens at 100°, melts at higher temperatures to a black mass, and burns with evolution of disagreeably smelling vapours. Dissolves easily in hot alcohol, and slightly in cold alcohol and ether (Bouis).

|  | *Over oil of vitriol.* |  |  |  | Saalmüller. *mean.* | Bouis. |
|---|---|---|---|---|---|---|
| 36 C | 216 | ........ | 53·33 | ........ | 54·03 | |
| 33 H | 33 | ........ | 8·14 | ........ | 8·27 | |
| 6 O | 48 | ........ | 11·85 | ........ | 14·18 | |
| Ag | 108 | ........ | 26·68 | ........ | 23·52 | ........ 26·6 |
| $C^{36}H^{33}AgO^6$ | ........ | 405 | ........ | 100·00 | ........ 100·00 | |

Saalmüller precipitates the salt from a strongly ammoniacal solution.

Ricinoleic acid dissolves in all proportions in *alcohol* and *ether* (Saalmüller).

## Ricinelaïdic Acid.

$$C^{36}H^{34}O^6 = C^{36}H^{34}O^2,O^4.$$
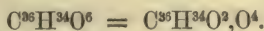
F. BOUDET. *J. Chim. méd.* 8, 646 ; *J. Pharm.* 18, 497 ; *Ann. Chim. Phys.* 50, 414 ; *Ann. Pharm.* 4, 16.
L. PLAYFAIR. *Phil. Mag.* 29, 475 ; *Mem. Chem. Soc.* 3, 222 ; *Ann. Pharm.* 60, 322 ; *J. pr. Chem.* 40, 173.
BOUIS. *N. Ann. Chim. Phys.* 44, 82.

*Palminsäure.*

*Formation.* Ricinoleic acid (the mixture of fatty acids obtained by saponifying castor oil with caustic soda and decomposing the soap) is mixed with nitric acid, and nitrous acid is passed into the mixture, whereupon the oil solidifies. Purification is effected by washing with hot water, crystallising repeatedly from alcohol, and pressing, till the

melting point becomes constant (Playfair). — 2. Ricinelaïdin is saponified with caustic potash, and the soap is salted out, decomposed by hydrochloric acid, and purified according to the first method (Boudet, Playfair).

*Properties.* Tufts of white silky needles, melting at 50° (Boudet. Bouis). When prepared according to the first method, it melts at 45—46°; according to the second, at 44·2° (Playfair). Solidifies at 48·5° (Bouis) to a crystalline mass (Playfair). Reddens litmus strongly (Boudet).

|  |  |  |  |  | Playfair. *mean.* |  |  |  | Bouis. |
|---|---|---|---|---|---|---|---|---|---|
| 36 C | 216 | ........ | 72·48 | ........ | 73·75 | ........ | 71·53 | ........ | 72·59 |
| 34 H | 34 | ........ | 11·41 | ........ | 11·85 | ........ | 11·50 | ........ | 11·50 |
| 6 O | 48 | ........ | 16·11 | ........ | 14·40 | ........ | 16·97 | ........ | 15·91 |
| C³⁶H³⁴O⁶ | 298 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

*a* was prepared according to 1; *b* by saponifying *a* and decomposing the soap. Playfair gave for *a* the formula C³⁴H³²O⁵; for *b*, C³⁴H³³O⁶. — Isomeric with ricinoleic acid (Gerhardt. Bouis).

Ricinelaïdic acid, subjected to rapid *distillation*, yields a buttery distillate, containing a large quantity of undecomposed acid and the same volatile oil which is produced by the dry distillation of castor oil: towards the end of the distillation, a yellow empyreumatic oil passes over, whilst a little charcoal remains behind (Boudet). When heated with hydrate of soda, it yields the same products as ricinoleic acid (Koch, *Ann. Pharm.* 119, 173; *Kopp's Jahresber.* 1861, 359).

Ricinelaïdic acid decomposes alkaline *carbonates.* The *ammonia-salt* is not crystallisable (Boudet).

*Potash-salt.* — Obtained by boiling the acid with a concentrated aqueous solution of carbonate of potash, dissolving the soap which separates on cooling, in alcohol, filtering from carbonate of potash, and evaporating (Playfair).

*Soda-salt.* — Formed by neutralising the acid with carbonate of soda. The alcoholic solution forms a jelly on cooling. A dilute aqueous solution deposits a bi-acid salt, which crystallises from alcohol in needles, and reddens litmus (Boudet).

*Baryta-salt.* — Obtained by precipitating the potash-salt with chloride of barium, and washing the precipitate with water and alcohol. — White powder, unctuous to the touch (Playfair).

|  |  |  |  | Playfair. |
|---|---|---|---|---|
| 36 C | 216 | ........ | 59·10 | 58·04 |
| 33 H | 33 | ........ | 9·03 | 9·09 |
| 5 O | 40 | ........ | 10·94 | 11·42 |
| BaO | 76·5 | ........ | 20·93 | 21·45 |
| C³⁶H³³BaO⁶ | 365·5 | ........ | 100·00 | 100·00 |

The *lime-salt* is soluble in boiling alcohol. — The *magnesia-salt*, obtained by dissolving magnesia in (alcoholic?) ricinelaïdic acid, has an alkaline reaction, and crystallises from the easily formed solution in warm alcohol in small laminæ, which melt below 100° (Boudet).

*Lead-salt.* — Oxide of lead forms with the acid a salt which is soluble in boiling alcohol, and separates from a concentrated solution in the form of a jelly, and from a dilute solution in needles (Boudet). Neutral acetate of lead precipitates from the soda-salt a basic salt of varying composition (Playfair).

*Copper-salt.* — Obtained by double decomposition as a fine green precipitate. It is less soluble in alcohol than the lime-salt, and separates from the solution in flocks on cooling. The salt is decomposed by prolonged boiling with alcohol, with separation of oxide of copper (Boudet).

*Silver-salt.* — Light, white powder, soluble in ammonia but insoluble in water, alcohol and ether (Playfair. Boudet).

|  |  |  |  |  | Playfair. |  | Bouis. |
|---|---|---|---|---|---|---|---|
| 36 C | 216 | ........ | 53·33 | ........ | 51·64 to 52·66 | ........ | 52·66 |
| 33 H | 33 | ........ | 8·14 | ........ | 8·12 „ 8·52 | ........ | 7·86 |
| 6 O | 48 | ........ | 11·85 | ........ |  |  | 12·48 |
| Ag | 108 | ........ | 26·68 | ........ | 27·36 „ 27·69 | ........ | 27·00 |
| $C^{36}H^{33}AgO^6$ | 405 | ........ | 100·00 |  |  |  | 100·00 |

The acid dissolves easily in *alcohol* and in *ether*.

*Appendix to Ricinoleic and Ricinelaïdic Acids.*

## 1. Castor Oil.

*Ricinusöl. Dünnes Palmöl.* From the seeds of *Ricinus communis* (*Handbuch* viii, *Phytochem.* 24). Concerning its preparation, see Planche (*Bull. Pharm.* 1, 241.)

Transparent, colourless or greenish-yellow, viscid oil. Sp. gr. at 19° = 0·96, constant in different samples (Bouis); 0·954 (Brandis); 0·9612 (Brisson); 0·9748 (Brandes & Reiche); 0·9699 at 12°, 0·9575 at 25°, 0·9081 at 94°, the sp. gr. of water at 15° being 1 (Saussure). Sp. gr. after separation of the stearin, 0·9369 at 21° (Scharling). Has a faint smell, and a mild, afterwards somewhat sharp taste. Acts as a purgative. — Without action on polarised light (Bouis & Silbermann). — Does not solidify at − 15° (Bouis). Solidifies at − 18° to a transparent yellow mass (Brandis). The oil obtained by expression, but not that obtained by boiling, deposits stearin in the cold (Boutron-Charlard, *J. Pharm.* 8, 392). See below. — Dissolves in all proportions in absolute alcohol (V. Rose, Bouis); in 1⅓ parts of alcohol of 36° (Bouis). Mixes with ether (Brande) and with chloride of ethyl (Pfaff).

|  |  | Saussure. |  | Ure. |  | Lefort. *mean.* |
|---|---|---|---|---|---|---|
| C | .... | 74·18 | ............ | 74·00 | ............ | 74·46 |
| H | .... | 11·03 | ............ | 10·29 | ............ | 11·41 |
| O | .... | 14·79 | ............ | 15·71 | ............ | 14·13 |
|  | .... | 100·00 | ............ | 100·00 | ............ | 100·00 |

The formula, $C^{56}H^{52}O^3$, proposed by Lefort, expresses the percentage composition, but not the decompositions of the oil. Castor oil, according to Tuson, contains small quantities of ricinine (p. 143).

When exposed to the air, castor oil becomes thicker and dries up, without turning opaque (Saussure, Bouis).

*Dry distillation.* Castor oil begins to boil about 265°, and yields a distillate consisting at first chiefly of a more volatile, afterwards of a less volatile, oil, without any great evolution of gas. After ⅓rd of the oil has passed over, the evolution of gas becomes more abundant, and the residue thickens without becoming coloured, and suddenly swells up to a spongy, elastic, caoutchouc-like mass, which fills the retort. 100 parts of the oil thus treated, yield 3 or 4 parts of a combustible gas (free from carbonic acid), 33 or 34 parts of distillate, and 62 to 64 parts of spongy residue (Bussy & Lecanu).

The formation of the spongy mass (see below) may be prevented by heating the oil very slowly from the beginning (Bouis). — The distillate consists of water, œnanthol (xii, 446) (Bussy), acetic, ricinic, and ricinoleic (p. 131) acids (Bussy & Lecanu). It contains, besides œnanthol, a little acrolein, œnanthylic acid (Bussy), and hydrocarbons, the last more particularly when the spongy mass is not formed (Bouis). When distilled with water, it yields œnanthol containing acrolein, from which crystals [of hydrate of œnanthol (xii, 448)?] separate on cooling to −18° (Bussy).

According to Stanek, the decomposition of castor oil takes place by two stages : *a.* Formation of (acrolein and) œnanthol. Probably thus :—

$$C^{36}H^{34}O^6 + 2HO = 2C^{14}H^{14}O^2 + 2C^4H^4O^2.$$
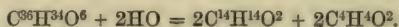
Ricinoleic acid.

In this reaction aldehyde must be formed, from which Bussy and Lecanu's acetic acid may have been produced. — *b.* Formation of the spongy residue.

$$C^{36}H^{34}O^6 = C^{36}H^{31}O^4 + 2HO + H \text{ (Stanek)}.$$
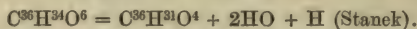
Pyroricinic
acid.

This explanation appears to me to be incorrect (Kr).

The vapours produced by heating castor oil are inflammable, and burn with a very bright flame. If the flame be extinguished, the same spongy mass remains which is formed by dry distillation. See Jonas (*N. Br. Arch.* 46, 168). — Castor oil is decomposed by the action of superheated steam at 160°, solid and liquid fatty acids being produced (Scharling, *J. pr. Chem.* 50, 377).

By the action of moist *chlorine* and *bromine,* chlorinated and brominated castor oil are formed. (See xvi, 316). *Brominated castor oil* is colourless when freshly prepared, but turns brown on heating ; it is a very thick liquid of sp. gr. 1·258 at 13·5°, containing 35·0 p. c. of bromine ($C^{56}H^{49}Br^3O^6$, according to Lefort). — *Chlorinated castor oil* is light-yellow, viscid, of sp. gr. 1·071 at 17·5°, and contains 19·65 p. c. of chlorine ($C^{56}H^{49}Cl^3O^6$) (Lefort, *N. J. Pharm.* 23, 349).

Castor oil gradually absorbs *sulphurous acid gas* on long exposure thereto ; the oil becomes thinner and after some time solidifies, from the formation of ricinelaïdin (Boudet). Saalmüller and Bouis were unable to obtain ricinelaïdin in this way ; oil saturated with sulphurous acid remained unchanged even after keeping for eight years (Bouis). Over mercury, castor oil absorbs 10 or 12 times its volume of sulphurous acid gas, which it gives up again completely to water (Saalmüller).

Castor oil dissolves in *oil of vitriol*, forming a yellow to yellowish-brown solution, which on addition of sugar [or acetic acid (A. Vogel)] and gentle warming, assumes a fine purple-violet colour, resembling that produced by gallic acid under similar conditions (Neukomm, *Ann. Pharm.* 116, 41; A. Vogel, *N. Jahrb. Pharm.* 3, 150). — The oil is not coloured by shaking with ⅕th of its volume of sulphuric acid of sp. gr. 1·635 or less (Calvert). — Its solution in absolute alcohol is decomposed by *hydrochloric acid gas*, with formation of glycerin and the vinic ethers of the fatty acids (Rochleder, *Ann. Pharm.* 59, 260). See vii, 239.

Castor oil in contact with *hyponitric* acid, solidifies more slowly than the (non-drying) fatty oils, but more quickly than rape oil, to a golden-yellow mass of ricinelaïdin (Boudet). The conversion is effected even by $\frac{1}{100}$th or less of hyponitric acid; it is brought about also by mercurous nitrate (Boudet), but more slowly, being complete only after some days (Davidson, *Ed. N. Phil. J.* 250; *J. pr. Chem.* 20, 235). After solidification a slow and regular evolution of nitrogen takes place, continuing for a month when a quantity of hyponitric acid equal to $\frac{1}{30}$th of the volume of the oil has been employed, and yielding a volume of nitrogen nearly equal to that of the oil (Boudet). — When mixed with one-third or half its volume of hyponitric acid, castor oil becomes hot, froths up, and turns opaque and viscid (Boudet). — The oil is not coloured by agitation with ⅕th of its volume of nitric acid of sp. gr. 1·33 or less; on the further addition of 10 volumes of caustic soda solution, it forms a ropy mass. When shaken with ⅕th of its volume of nitro-sulphuric acid (composed of equal volumes of sulphuric acid of sp. gr. 1·845 and nitric acid) it assumes a brown-red colour in two minutes (Calvert, *J. pr. Chem.* 61, 354). — When heated with dilute *nitric acid*, it froths up strongly, and on continued distillation yields œnanthylic acid (xii, 451), whilst a thick fatty oil still containing œnanthylic acid, remains in the retort, together with nitric acid holding suberic and oxalic acids in solution (Tilley, *Ann. Pharm.* 39, 160). Besides these, azelaic acid is produced, but no sebacic acid (Arppe, *Ann. Pharm.* 120, 288; 124, 98). When the oil is very slowly heated with dilute nitric acid, a large quantity of hydrocyanic acid is given off, and, on cooling the mixture before the formation of suberic acid takes place, it deposits hard, fern-like crystals of an acid soluble in water and alcohol. This body melts when heated, giving off acid vapours, and forms a baryta-salt soluble in a large quantity of water, and a silver-salt which explodes when heated. It contains, on an average, 20·92 p. c. C., 10·34 N., 4·39 H., and 64·35 O., corresponding to the formula $C^{14}X^2H^{17}O^{20}$ (21·05 C., 10·52 N., 4·26 H., and 64·17 O.) (Bouis).

By the action of *chloride of lime* on castor oil, chloroform is obtained (Chautard). — The oil, heated with *bichromate of potash* and dilute sulphuric acid, yields œnanthylic acid and a neutral volatile oil having the composition of valeric aldehyde (xi, 17) (Arzbächer, *Ann. Pharm.* 73, 200). When it is digested or heated with alcoholic *ammonia*, ricinolamide (p. 147) is produced (Boullay; Bouis).

Castor oil is easily saponified by heating with aqueous *alkalis*; it yields 8 p. c. of glycerin and (on decomposing the soap) 94 p. c. of oily fatty acids, the latter consisting of ricinoleic acid with a small quantity of solid fatty acids (Bussy & Lecanu). See the decomposition with excess of alkali, under *Ricinoleic acid* (p. 133).

Concerning *the solid fatty acids of castor oil*, varying statements have

been made: *a.* According to Bussy & Lecanu, the oily mixture of fatty acids deposits, at 15° to 18°, $\frac{1}{5}$th at most of an acid melting at 130° (Bussy & Lecanu's margaritic acid), and afterwards, at 10° to 12°, ricinic acid melting at 22°. *Margaritic acid*, after re-crystallising and pressing, forms pearly laminæ containing 70·5 p. c. C., 10·9 H., and 18·6 O.; it distils partly undecomposed, is more difficultly soluble in alcohol than margaric acid, and forms a magnesia-salt insoluble in alcohol. — *Ricinic acid*, which is obtained also by the distillation of castor oil, is white and pearly; it solidifies in a crystalline mass after fusion, and distils almost without decomposition. It contains 73·56 p. c. C., 9·86 H., and 16·58 O., and dissolves very easily in alcohol and ether. The magnesia-salt prepared with one part of magnesia and two parts of the acid, when dissolved in alcohol, turns reddened litmus blue; it is not perceptibly soluble in water, but dissolves easily in alcohol, and crystallises therefrom in white, shining needles. The lead-salt, which has an alkaline reaction, is very easily soluble in alcohol. This behaviour of the salts distinguishes ricinic acid from other fatty acids (Bussy & Lecanu). — *b.* According to Saalmüller, the solid acids are separated with difficulty by exposing crude ricinoleic acid to a temperature of — 10° or — 12°, but more easily and completely after the addition of $\frac{1}{3}$rd of the volume of alcohol. The laminæ which separate exhibit the melting-point of margaric acid only when they are contaminated with alkali. After purification they melted *on one occasion* at 74°, solidifying again at 68° to 70°, and contained 76·85 p. c. C., 12·74 H., and 10·41 O., and might therefore be regarded as stearic acid. On a *second* occasion they had, with the same melting-point (74°), the composition of palmitic acid (*mean:* 74·66 p. c. C., 12·65 H., and 12·69 O.). On a *third* occasion white granules and tables, melting at 51° (after distillation at 54°), were obtained from the spontaneously formed deposit in castor oil, their composition, according to analyses which were not concordant, being represented by the formula $C^{60}H^{59}O^5$, and that of the potash- and silver-salts by $C^{60}H^{57}M^2O^5$. Saalmüller invariably found only one acid, not susceptible of further decomposition (*Ann. Pharm.* 64, 108. — *Sill. Am. J.* [2] 8, 263; *Kopp's Jahresber.* 1850, 403). — *c.* Castor oil, when kept in large quantities, deposits a solid fat, which, after repeated treatment with alcohol, melts at 44°, and solidifies to a waxy mass. By saponifying this body, and decomposing the soap, an acid is obtained which melts at 72°, and cannot be decomposed by re-crystallisation from alcohol. The acid may be obtained of the same melting-point by converting the expressed oil into lead-salts and removing the portion soluble in ether. Its solution in 50 parts of boiling alcohol solidifies almost completely at 12°. It contains 74·05 p. c. C., 13·18 H., and 12·77 O.; in the silver-salt 52·39 p. c. C., 9·35 H., 29·40 Ag., and 8·86 O.; and has, therefore, with the melting-point of stearic acid, the composition of palmitic acid; it is, however, more volatile than stearic acid, and must be regarded as a peculiar acid (Scharling, *J. pr. Chem.* 45, 434).

## 2. *Oil of Jatropha Curcas* (*Handbuch* viii [2], 24.)

*Oleum Ricinum.* Colourless oil of sp. gr. 0·91 at 19°. Inodorous, and of mild taste. Solidifies to a buttery mass at — 8°. — Absorbs oxygen slowly from the air. When heated it yields acrolein, sebacic

acid, and other products. When saturated with sulphurous acid gas, and set aside for three months, it deposits crystalline nodules of an acid, which, after crystallisation from alcohol, melts at 58° and has the composition of isocetic acid (xvi, 365). — The oil carbonises with oil of vitriol at 110°. Hyponitric acid renders it pasty, but not quite solid. — Nitric acid evolves nitric oxide and hydrocyanic acid, sets free solid fatty acids, and ultimately forms suberic acid. — With alcoholic ammonia the oil forms isocetamide (xvi, 365). — It is nearly insoluble in alcohol. — Saponifies slowly with caustic potash, and quickly with caustic soda, forming a white hard soap, containing isocetic acid and a fluid oleic acid of the formula $C^{36}H^{34}O^{6}$, which does not solidify at − 10°, and forms two lead-salts soluble in ether, $C^{36}H^{33}PbO^{6}$, and $2C^{36}H^{23}O^{5}$, (PbO,HO) (Bouis, *Compt. rend.* 39, 923; *Pharm. Centr.* 1854, 913; *Chem. Gaz.* 1854, 469). Since, according to Arnaudon & Ubaldini (*Kopp's Jahresber.* 1858, 536), the oil yields caprylic alcohol when heated with hydrate of potash, the fluid oleic acid may doubtless be regarded as ricinoleic acid.

3. *Oil of the fruit of Jatropha glauca and J. glandulifera.*—Yellow, of sp. gr. 0·963; solidifying at 5° (Lepine).

## 4. *Spongy Residue from the dry distillation of Castor Oil.*

Bussy & Lecanu. *J. Pharm.* 13, 57.
Stanek. *J. pr. Chem.* 63, 138.
Bouis. *N. Ann. Chim. Phys.* 44, 80.

When the residue left in the distillation of castor oil (according to p. 138), is freed from acrolein and residual oil, by means of alcohol (Bussy & Lecanu), alcohol and ether (Stanek), or water and alcohol (Bouis), there remains an elastic, pale-yellow, inodorous and tasteless mass, which is somewhat friable after drying (Bussy & Lecanu).

This mass dried at 100° contains on an average, 77·15 p. c. C., 10·77 H., and 12·08 O., corresponding to the formula $C^{42}H^{34}O^{5}$ (by calc. 77·30 p. c. C., 10·42 H., and 12·28 O.), and from its behaviour with caustic potash, is to be regarded as pyroricinate of acryl (Stanek). It contains 73·2 p. c. C., 10·9 H., and 15·9 O., agreeing with the formula $C^{36}H^{32}O^{6}$ (by calc. 72·97 p. c. C., 10·81 H., and 16·22 O.); it is saponifiable, and forms a silver-salt soluble in ammonia, and a baryta-salt, $C^{36}H^{31}BaO^{6}$, containing 21 p. c. baryta, insoluble in water, alcohol, and ether (Bouis).

The spongy mass decomposes when *heated*, without softening [with formation of acrolein (Stanek)], and with access of air *burns* slowly, with a bright, slightly smoky flame. — It is not perceptibly acted on by *nitric acid, oil of vitriol,* or *hydrochloric acid* (Bussy & Lecanu). By saponification with strong caustic *potash* it is resolved into pyro-ricinic acid and a brown resin, evolving at the same time an odour of aldehyde-resin. Stanek regards the body formed in this reaction, as a compound of acrolein ($C^{42}H^{34}O^{5} = C^{36}H^{30}O^{3},C^{6}H^{4}O^{2}$). It is not acted upon by dilute caustic potash (Bussy & Lecanu).

Insoluble in *alcohol, ether,* and *volatile and fatty oils,* even when boiling (Bussy & Lecanu).

## 5. Pyroricinic Acid.

*Aporicinic acid* (Berzelius).   Previously observed by Bussy and Lecanu.

*Formation.*   (P. 138.)

*Preparation.*   Castor oil is distilled in a retort over an open fire, till the residue swells up, with evolution of gas ; and the residue, after cooling, is treated with alcohol and with ether and alcohol in succession, to remove substances soluble in those menstrua.   The undissolved portion, Stanek's pyroricinate of acryl (p. 141), is saponified with caustic potash, salted out, and converted into a lime-salt by dissolving the soap in water and precipitating with chloride of calcium.   The lime-salt is extracted by ether, and decomposed by hydrochloric acid ; the precipitate is again dissolved in caustic potash, and precipitated with neutral acetate of lead ; the lead-salt is decomposed under alcohol by hydrosulphuric acid ; and the solution, filtered from sulphide of lead, is mixed with water, and the alcohol driven off.

After several hours' drying at 100°, it forms a semi-fluid, amber-yellow, or brownish mass, of peculiar odour.   On further drying it loses more water, and after three days' exposure to a temperature of 100°, contains 82·5 p. c. C., corresponding to the formula $C^{36}H^{29}O^2$ (Stanek).

|  | *Dried at* 100° *for several hours.* |  |  | Stanek. |
|---|---|---|---|---|
| 36 C | 216 | | 70·59 | 70·4 |
| 34 H | 34 | | 11·11 | 11·0 |
| 7 O | 56 | | 18·30 | 18·6 |
| $C^{36}H^{34}O^7$ | 306 | | 100·00 | 100·0 |

Stanek's formula.   From the analysis of the lead-salt he considers the acid to be $C^{36}H^{31}O^4$.

*Decompositions.*   By *drying* (see above). — The freshly prepared lime-soap, when heated to 260° with excess of *soda-lime*, leaves a residue (free from sebacic acid) from which sulphuric acid sets free caprylic acid.

Pyroricinic acid is insoluble in *water*. — It forms with *magnesia* a salt insoluble in water and alcohol (Bussy and Lecanu).

*Lead-salt.*   Preparation, see above.   Perfectly insoluble in alcohol and ether.

|  | *At* 100°. |  |  | Stanek. |
|---|---|---|---|---|
| 36 C | 216 | | 56·58 | 56·65 |
| 30 H | 30 | | 7·86 | 7·66 |
| 3 O | 24 | | 6·29 | 7·05 |
| PbO | 111·8 | | 29·27 | 28·64 |
| $C^{36}H^{30}PbO^4$ | 381·8 | | 100·00 | 100·00 |

Pyroricinic acid dissolves in weak *alcohol* less freely than oleic acid (Bussy & Lecanu, *J. Pharm.* 13, 57).

## 6. Ricinine.

Tuson. *Chem. Soc. J.* 17, 195; *Chem. News,* 9, 209; *Zeitschr. Ch. Pharm.* 7, 309.

An alkaloïd contained in castor-seeds. Croton seeds contain a similar base, perhaps the same.

*Preparation.* The bruised seeds are exhausted by repeated boiling with water; the decoction is strained; and after separating the oil as completely as possible, it is evaporated to an extract, which is boiled with alcohol and filtered. After standing for 24 hours, the tincture is separated from the deposited resin, and the alcohol is distilled off. The residue, on standing, deposits crystals of ricinine, which are purified by re-crystallisation from alcohol, with the help of charcoal.

*Properties.* Colourless, rectangular prisms and laminæ, having a slight taste of bitter almonds. When heated it melts to a colourless liquid, which solidifies in crystalline needles. Sublimes unchanged between two watch-glasses. Contains nitrogen.

*Burns* when strongly heated on platinum foil with a luminous smoky flame. Dissolves in *oil of vitriol* without coloration; the solution is coloured green by chromate of potash. — Dissolves in *nitric acid* without evolving red fumes, and on evaporation leaves colourless needles, which turn white in water.

Ricinine is insoluble in *water*. — It forms with *hydrochloric acid,* a compound which is decomposed by evaporating the solution. — Its solution, mixed with *mercuric chloride*, solidifies after some minutes to a crystalline mass of fine needles. — The hydrochloric acid solution, when evaporated with *chloride of platinum*, yields orange-coloured octahedra of the double-salt.

Ricinine is soluble in *alcohol,* and nearly insoluble in *ether* and *benzene.*

## Ricinoleate of Ethyl.

$$C^{40}H^{38}O^6 = C^4H^5O, C^{36}H^{33}O^5.$$
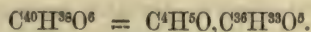
Saalmüller. *Ann. Pharm.* 64, 123.

*Ricinölvinester.*

Formed by passing hydrochloric acid gas into an alcoholic solution of ricinoleic acid [into alcoholic castor oil (Rochleder, *Ann. Pharm.* 59, 260)], and purified by precipitating with water, and washing with alkaline and pure water.

Wine-yellow oil, not volatile without decomposition.

|  |  |  |  | | Saalmüller. |
|---|---|---|---|---|---|
| 40 C | 240 | ........ | 73·62 | ........ | 73·87 |
| 38 H | 38 | ........ | 11·66 | ........ | 11·76 |
| 6 O | 48 | ........ | 14·72 | ........ | 14·37 |
| $C^4H^5O, C^{36}H^{33}O^5$ | 326 | ........ | 100·00 | ........ | 100·00 |

## Ricinelaïdate of Ethyl.

$$C^{40}H^{38}O^6 = C^4H^5O,C^{36}H^{33}O^5.$$
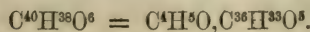
PLAYFAIR. *Phil. Mag.* 29, 479.

Formed by the action of hydrochloric acid gas on alcoholic ricinelaïdic acid.

Melts at 16 °(Playfair. Bouis).—Dissolves slightly in cold, and very freely in hot alcohol.

|  |  |  |  |  | Playfair. *mean.* |
|---|---|---|---|---|---|
| 40 C | 240 | ........ | 73·62 | ........ | 72·43 |
| 38 H | 38 | ........ | 11·66 | ........ | 12·13 |
| 6 O | 48 | ........ | 14·72 | ........ | 15·44 |
| $C^4H^5O,C^{36}H^{33}O^5$ | 326 | ........ | 100·00 | ........ | 100·00 |

## Ricinelaïdin.

$$C^{78}H^{72}O^{14} = C^6H^6O^4,2C^{36}H^{33}O^5.$$
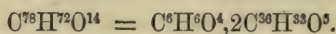
*Literature;* see under Ricinelaïdic acid (p. 135).

*Palmin.* Discovered by Boudet.

*Formation.* 1. From castor oil and hyponitric acid (p. 139). — 2. From castor oil and sulphurous acid (p. 138).

*Preparation.* Hyponitric acid gas is passed into castor oil; or the oil is shaken with 3 p. c. of its weight of nitric acid saturated with nitrous acid, whereupon the oil is coloured reddish and converted into a solid mass, sometimes yellow, brittle, and waxy, sometimes translucent and glassy. It is purified by washing with water and crystallising from alcohol (Bouis), or ether (Playfair).

Small white nodules (Bouis). Opaque, amorphous granules (Playfair). Melts at 43° (Playfair), 45° (Bouis), 62° to 66° (Boudet). Solidifies slowly, remaining pasty for a long time.

|  |  |  |  |  | Playfair. *mean.* |  | Bouis. *mean.* |
|---|---|---|---|---|---|---|---|
| 78 C | 468 | ........ | 71·78 | ........ | 72·95 | ........ | 71·45 |
| 72 H | 72 | ........ | 11·04 | ........ | 11·49 | ........ | 11·07 |
| 14 O | 112 | ........ | 17·18 | ........ | 15·56 | ........ | 17·48 |
| $C^6H^6O^4,2C^{36}H^{33}O^5$ | 652 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Playfair proposed the formula $C^{37}H^{34}O^6$; Bouis, the one above.

*Decompositions.* Impure ricinelaïdin turns brown in the *air* (Bouis). —When submitted to dry distillation it behaves like castor oil, yielding a dark, brown-red spongy residue, a distillate containing œnanthol (Bertagnini, *Ann. Pharm.* 85, 282), and an oily acid, fluid at 0°, but no ricinelaïdic acid (Boudet). If the œnanthol be driven off from the dis-

tillate by means of steam there remains a solid acid, containing 73·82 p. c. C., and 11·21 H. (Bouis). — With care the distillation may be continued to the end without the formation of the spongy residue, in which case a large quantity of acrolein and solid hydrocarbons pass over, whilst a little carbon remains behind (Bouis). Ricinelaïdin is saponifiable, though less easily than castor oil; it diffuses thereupon an odour of volatile oil (Boudet). — By distillation with excess of *hydrate of potash* it yields caprylic alcohol, sebate of potash, and two other acids (Bouis).

Ricinelaïdin dissolves slightly in cold *alcohol* (Playfair); in 2 parts of alcohol of 36 gr. at 30°, and still more freely in boiling alcohol (Boudet). It is easily soluble in *ether* (Boudet).

*Bromine-nucleus* $C^{36}BrH^{35}$.

## Bromostearic Acid.

$$C^{36}BrH^{35}O^4 = C^{36}BrH^{35},O^4.$$
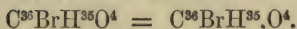
A. C. OUDEMANNS, Jun. *J. pr. Chem.* 89, 193.

Stearic acid (7 parts) is heated with water and bromine (4 parts), in a sealed tube, to 130° or 140° at most, till the brown colour of the bromine disappears, and the mixture assumes the appearance of a yellow oil, cooling to a crystalline solid. After washing away the hydrobromic acid, the contents of the tube are dissolved in 20 times their weight of warm alcohol of 80 p. c., and the unchanged stearic acid is separated by cooling to − 10°. The liquid is then mixed with an equal volume of water and an excess of crystallised carbonate of soda, and evaporated to dryness over the water-bath. The tough saline mass thus obtained is boiled with 10 volumes of alcohol of 80 p. c., and filtered as hot as possible; and the crystals of bromostearate of soda which form in the filtrate (and of which more may be obtained by evaporating the solution), are collected and purified by repeated crystallisation from alcohol. The mother-liquor contains bibromostearate of soda.

From the soda-salt the bromostearic acid is separated by dilute sulphuric acid.

*Properties.* Yellow, indistinctly crystalline mass, melting at 41°, and of sp. gr. 1·0653 at 20°.

Bromostearic acid is very slowly decomposed by heating with excess of *caustic potash*. — Bromostearate of silver, heated with water, forms bromide of silver and stearidic acid $C^{36}H^{34}O^4$ (p. 78).

The acid is insoluble in *water*. It forms with the alkalis soap-like compounds, which crystallise from alcohol.

*Bromostearate of Potash* is more soluble than the soda-salt.

*Bromostearate of Soda.* — Preparation described above.

|  |  |  |  | Oudemanns. mean. |  |
|---|---|---|---|---|---|
| 36 C........................ | 216 | ........ | 56·10 | ........ | 55·90 |
| Br ..................... | 80 | ........ | 20·78 | ........ | 21·08 |
| 34 H ...................... | 34 | ........ | 8·83 | ........ | 8·87 |
| 3 O........................ | 24 | ........ | 6·24 | ........ | 6·22 |
| NaO .......................... | 31 | ........ | 8·05 | ........ | 7·93 |
| C$^{36}$BrH$^{34}$NaO$^4$ .... | 385 | ........ | 100·00 | ........ | 100·00 |

The bromostearates of the alkalis precipitate *metallic salts.*
The acid dissolves easily in *alcohol* and *ether.*

*Bromine-nucleus* C$^{36}$Br$^2$H$^{34}$.

## Bibromostearic Acid.

$$C^{36}Br^2H^{34}O^4 = C^{36}Br^2H^{34},O^4.$$
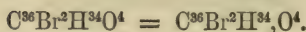
OUDEMANNS. *J. pr. Chem.* 89, 193.

Formed, in the preparation of bromostearic acid, by heating bromine with stearic acid (p. 145), and obtained in the form of an uncrystallisable soda-salt. The salt is brown, tenacious, very hygroscopic, dissolves easily in alcohol, and forms with water an opaque, soapy solution. After drying at 130° it contains 32·5 p. c. of bromine, and 6·59 of soda, approximating to the formula C$^{36}$Br$^2$NaH$^{33}$O$^4$ (calc. 34·7 p. c. Br. 6·68 NaO).

*Chlorine-nucleus* C$^{36}$Cl$^{10}$H$^{26}$.

## Chlorostearic Acid.

$$C^{36}Cl^{10}H^{26}O^4 = C^{36}Cl^{10}H^{26},O^4.$$
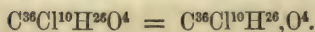
HARDWICK. *Chem. Soc. Qu. J.* 2, 232 ; *Ann. Pharm.* 72, 270.

*Chlorbassinsaüre.* See xvi, 365.

Stearic acid at 100° is treated with dry chlorine, whereupon it first becomes thicker, and is ultimately converted into a solid resin.

|  |  |  |  | Hardwick. mean. |  |
|---|---|---|---|---|---|
| 36 C........................ | 216 | ........ | 34·06 | ........ | 34·37 |
| 10 Cl ...................... | 355 | ........ | 56·78 | ........ | 57·16 |
| 26 H........................ | 26 | ........ | 4·10 | ........ | 4·37 |
| 4 O ........................ | 32 | ........ | 5·06 | ........ | 4·10 |
| C$^{36}$Cl$^{10}$H$^{26}$O$^4$ ........ | 629 | ........ | 100·00 | ........ | 100·00 |

Forms with *potash* an amorphous soap, which does not crystallise from alcohol. The *baryta-* and *lead-salts* are insoluble in water.

*Amidogen-nucleus* $C^{36}AdH^{35}$.

## Stearamide.

$$C^{36}NH^{37}O^2 = C^{36}AdH^{35},O^2.$$
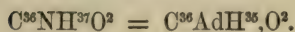
H. Carlet. *Par. Soc. Bull.* (1859) 1, 76.

Obtained in the same manner as palmitamide (xvi, 382). After melting it solidifies at 107·5°, but is probably still impure. The acid separated from the amide by alcoholic potash melts at 69·5°.

| | | | | | | | Carlet. | |
|---|---|---|---|---|---|---|---|---|
| 36 C | ................... | 216 | ........ | 76·33 | ........ | 74·92 | ........ | 75·74 |
| N | ................... | 14 | ........ | 4·94 | | | 5·00 | |
| 37 H | ................... | 37 | ........ | 13·07 | ........ | 11·87 | ........ | 13·90 |
| 2 O | ................... | 16 | ........ | 5·66 | | | | |
| $C^{36}NH^{37}O^2$ | ........ | 283 | ........ | 100·00 | | | | |

## Stearanilide.

$$C^{48}NH^{41}O^2 = C^{36}(NH.C^{12}H^5)H^{35},O^2.$$
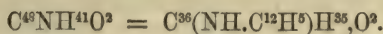
Pebal. *Ann. Pharm.* 91, 151.

When an excess of aniline is distilled over stearic acid heated to 230° in an oil-bath, the whole of the stearin is converted into anilide. The product is purified by repeated crystallisation from alcohol.

$$C^{36}H^{36}O^4 + C^{12}NH^7 = C^{48}NH^{41}O^2 + 2HO.$$
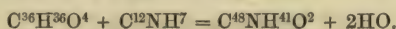
White, delicate, shining needles, melting at 93·6°, and solidifying to a mass of radiated crystals. — An alcoholic solution does not precipitate nitrate of silver.

| | | | | | Pebal. *mean.* |
|---|---|---|---|---|---|
| 48 C | ............... | 288 | ........ | 80·22 | 80·00 |
| N | ............... | 14 | ........ | 3·90 | |
| 41 H | ............... | 41 | ........ | 11·42 | 11·57 |
| 2 O | ............... | 16 | ........ | 4·46 | |
| $C^{48}NH^{41}O^2$ | .... | 359 | ........ | 100·00 | |

*Oxy-amidogen-nucleus* $C^{36}AdH^{33}O^2$.

## Ricinolamide.

$$C^{36}NH^{35}O^4 = C^{36}AdH^{33}O^2,O^2.$$
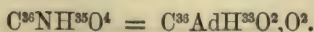
Boullay. *N. J. Pharm.* 5, 329; abstr. *Compt. rend.* 32, 223.
Bouis. *Compt. rend.* 33, 144; *Ann. Pharm.* 80, 304; *J. pr. Chem.* 54, 46; *Pharm. Centr.* 1851, 796; Complete: *N. Ann. Chim. Phys.* 44, 96.

Discovered by Boullay in 1843.

*Formation and Preparation.* An alcoholic solution of castor oil saturated with ammoniacal gas, is allowed to stand for three or four months, or heated for three to four days in a bath of chloride of sodium. The product obtained by expressing and evaporating the alcoholic mother-liquor is purified by crystallising from alcohol, precipitating the alcoholic solution with water, and again crystallising from alcohol.

*Properties.* White crystalline nodules, melting to a transparent liquid at 66°. Solidifies to an opaque, brittle mass.

|  |  |  |  |  | Bouis. |
|---|---|---|---|---|---|
| 36 C ............... | 216 | ........ | 72·72 | ........ | 69·51 to 73·36 |
| N ............... | 14 | ........ | 4·71 | ........ | 4·00 „ 4·74 |
| 35 H............... | 35 | ........ | 11·78 | ........ | 11·40 „ 12·09 |
| 4 O ............... | 32 | ........ | 10·79 | ........ |  |
| $C^{36}NH^{35}O^4$ .... | 297 | ........ | 100·00 |  |  |

*Decompositions.* 1. *Burns* with a smoky flame. — 2. Dissolves in *oil of vitriol* with red colour. — 3. Decomposed by *dilute acids*, without coloration, into ammonia-salt and ricinoleic acid. — With hot strong solution of caustic potash, it evolves ammonia, and forms ricinoleate of potash, which at higher temperatures is decomposed into a salt of sebacic and caprylic alcohol (p. 133).

*Combinations.* Ricinolamide is insoluble in *water*, but soluble in *alcohol* and *ether*.

## Ricinelaïdamide.

$$C^{36}NH^{35}O^4 = C^{36}AdH^{33}O^2,O^2.$$
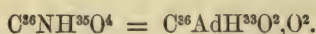
ROWNEY. *Chem. Gaz.* 1855, 361; *J. pr. Chem.* 67, 157.

Obtained by the action of ricinelaïdin on alcoholic ammonia. Closely resembles elaïdamide. Melts at 91–93°, and solidifies at 89°.

|  |  |  |  |  | Rowney. mean. |
|---|---|---|---|---|---|
| 36 C............... | 216 | ........ | 72·72 | ........ | 72·78 |
| N ............ | 14 | ........ | 4·71 | ........ | 4·79 |
| 35 H ............ | 35 | ........ | 11·78 | ........ | 11·91 |
| 4 O ............ | 32 | ........ | 10·79 | ........ | 10·52 |
| $C^{36}NH^{35}O^4$ .... | 297 | ........ | 100·00 | ........ | 100·00 |

# COMPOUNDS CONTAINING 38 ATOMS OF CARBON.

*Primary Nucleus* $C^{38}H^{20}$; *Oxygen-nucleus* $C^{38}H^{14}O^6$.

## Vulpic Acid.

$$C^{38}H^{14}O^{10} = C^{38}H^{14}O^6,O^4.$$
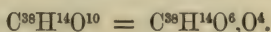
F. Möller & A. Strecker. *Ann. Pharm.* 113, 56; abstr. *Chem. Centr.*
1860, 225; *J. pr. Chem.* 79, 468; *N. Ann. Chim. Phys.* 58, 486.
W. Stein. *Zeitschr. Ch. Pharm.* 7, 97; *N. Br. Arch.* 118, 230; *Zeitschr.
Ch. Pharm.* 8, 47; *J. pr. Chem.* 93, 366.
Bolley & Kinkelin. *Zürich. Mitth.* 1865, 1; *J. pr. Chem.* 93, 354.

*Vulpulin.* Discovered by Bebert (*J. Pharm.* 17, 696) in *Cetraria vulpina*, but
imperfectly described by him, so that it was regarded by Berzelius and Gerhardt as
identical with chrysophanic acid (xvi, 171): investigated by Möller and Strecker. —
Stein found in *Parmelia parietina* [growing, not on trees, like that of Rochleder and
Heldt (xvi, 172), but on a sandstone rock], instead of chrysophanic acid, his
*chrysopicrin*, which was afterwards recognised by Bolley, Strecker, and Stein him-
self, as vulpic acid: the *resinous wall-lichen yellow* of Schrader, and the *Parmelia
yellow* of Herberger may, therefore, also be identical with vulpic acid. See xvi, 171.

*Preparation.* 1. Extracted from the wall-lichen by sulphide of
carbon in a nearly pure state (Stein). — 2. One part of *Cetraria vulpina*
is digested with 20 parts of luke-warm water and a little milk of lime.
After standing six hours the liquid is strained, and the residue treated
afresh with the same quantity of water and milk of lime. The mixed
extracts are then supersaturated with hydrochloric acid, and the
precipitated flocks are washed with cold water, and purified by
crystallisation from boiling water or alcohol (Möller & Strecker).
Boiling water acts prejudicially in the extraction. — Chloroform also
(Möller & Strecker) and alcohol (Bebert) extract the vulpic acid from
the cetraria.

*Properties.* Large sulphur-yellow, transparent, pyramids or needles
belonging to the oblique prismatic system (Möller & Strecker;
Bolley). When crystallised from sulphide of carbon, it possesses the
colour of bichromate of potash; from alcohol it is less red. Acids
precipitate it of a yellow colour from alkaline solutions (Stein). Melts
above 100° (Möller & Strecker), at 110° (Bolley), 140° (Stein), and
solidifies in a crystalline mass. Sublimes at 120° in small yellow
laminæ (Bolley), in long needles having an odour of benzoin. Taste-
less alone, but very bitter in alcoholic solution (Stein).

|  |  |  |  | Möller and Strecker. |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | mean. |  | Bolley. |  | Stein. |
| 38 C ............... | 228 | ........ | 70·81 | ........ | 70·63 | ........ 70·74 | ........ | 70·69 |
| 14 H ............... | 14 | ........ | 4·35 | ........ | 4·33 | ........ 4·56 | ........ | 4·41 |
| 10 O ............ | 80 | ........ | 24·84 | ........ | 25·04 | ........ 24·70 | ........ | 24·90 |
| $C^{38}H^{14}O^{10}$ ........ | 322 | ........ 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Former $C^{30}H^{10}O^8$, according to Stein.

*Decompositions.* 1. Vulpic acid decomposes when *heated*, evolving

yellow fumes which condense in powder and in drops, and leaving a large quantity of charcoal. — 2. When boiled with excess of *caustic potash*, it takes up 6 atoms of water, and is converted into oxatolylic acid, carbonic acid, and methylic alcohol:

$$C^{38}H^{14}O^{10} + 6HO = C^{32}H^{16}O^6 + 4CO^2 + C^2H^4O^2.$$
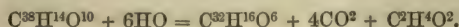
3. By boiling with *baryta-water* it is resolved into oxalic acid, methylic alcohol, and alphatoluic acid:

$$C^{38}H^{14}O^{10} + 8HO = 2C^{16}H^8O^4 + C^4H^2O^8 + C^2H^4O^2 \text{ (Möller and Strecker)}.$$
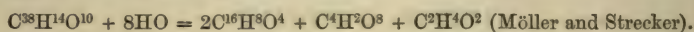
Bolley obtained oxalic acid, but instead of methylic alcohol, oily drops having an odour of bitter almonds. — 4. *Sodium-amalgam* decolorises the alkaline solution, whereupon hydrochloric acid throws down a green-yellow body, resembling tannic acid in its behaviour with tartar emetic and sesquichloride of iron. — 5. Solution of *chloride of lime* forms with it a red amorphous resin, and a volatile oil having an odour of bitter almonds, apples, and cinnamon. A similar effect is produced by heating it to 160° for 12 hours with water containing sulphuric acid. — 6. The acid does not reduce *potassio-cupric tartrate* even on boiling with acids or alkalis (Stein).

*Combinations.* Vulpic acid is nearly insoluble in *water*, even when boiling. It assumes a deep-red colour with *oil of vitriol*, and forms a brown-red solution, which is changed to pale-yellow by the addition of water (Bolley).

The acid combines with bases to form salts having the formula C$^{38}$MH$^{18}$O$^{10}$. The vulpates of the alkalis and alkaline earths are crystallisable; those of the heavy metals insoluble in water. The acid expels carbonic acid from alkaline carbonates (Möller & Strecker).

*Ammonia-salt.* The solution of the acid in warm aqueous ammonia deposits, on cooling, yellow needles, which give off water and ammonia when heated, and afterwards are not completely soluble in water (Möller & Strecker).

|  |  | *Air-dried.* |  | Möller and Strecker. |  |
|---|---|---|---|---|---|
| 38 C | 228 | ........ | 63·84 | ........ | 64·38 |
| N | 14 | ........ | 3·92 | ........ | 4·13 |
| 19 H | 19 | ........ | 5·32 | ........ | 5·11 |
| 12 O | 96 | ........ | 26·92 | ........ | 26·38 |
| C$^{38}$(NH$^4$)H$^{18}$O$^{10}$ + 2 aq. | 357 | ........ | 100·00 | ........ | 100·00 |

*Potash-salt.* — The acid is dissolved in aqueous carbonate of potash, or its alcoholic solution is shaken with the dry carbonate (Möller & Strecker). Stein adds vulpic acid to boiling alcoholic potash till it ceases to dissolve. — Bright-yellow needles, losing 4·8 p. c. (Möller & Strecker), 4·74 p. c. (Stein) of water at 100° (2 at. = 4·8 p. c.). Difficultly soluble in water and alcohol.

|  |  | *Dried.* |  | Möller and Strecker. | | Stein. |
|---|---|---|---|---|---|---|
| 38 C | 228 | ........ | 63·30 | ........ | 63·64 | |
| 13 H | 13 | ........ | 3·61 | ........ | 3·61 | |
| 9 O | 72 | ........ | 19·99 | ........ | 20·11 | |
| KO | 47·2 | ........ | 13·10 | ........ | 12·64 | ........ | 12·9 |
| C$^{38}$KH$^{13}$O$^{10}$ | 360·2 | ........ | 100·00 | ........ | 100·00 | |

*Baryta-salt.* — When vulpic acid is boiled with moist carbonate of baryta, pale-yellow needles are obtained on cooling. By re-crystallisation from boiling alcohol they are converted into orange-coloured crystals, or a mixture of lighter and darker crystals, containing variable proportions of water. The paler crystals lose 14·1 p. c. of water at 100° (7 at. = 13·9 p. c. HO) (Möller & Strecker). Similar observations were made also by Stein.

| | | Dried. | | | Möller and Strecker. |
|---|---|---|---|---|---|
| 38 C | ...... | 228 | ........ | 58·52 | 58·40 |
| 13 H | ...... | 13 | ........ | 3·33 | 3·52 |
| 9 O | ...... | 72 | ........ | 18·49 | 18·68 |
| BaO | ...... | 76·6 | ........ | 19·66 | 19·40 |
| $C^{38}BaH^{13}O^{10}$ | .... | 389·6 | ........ | 100·00 | 100·00 |

Bolley found 20·05 p.c. of baryta; Stein 18·56 p.c. of baryta and 14·06 p.c. of water.

Alcoholic solution of vulpic acid does not precipitate *neutral acetate of lead;* it renders the *basic acetate* cloudy, and produces a sulphur-yellow precipitate. — The acid colours *sesquichloride of iron* a deeper yellow (Stein; Bolley).

*Silver-salt.* — Nitrate of silver throws down from the soda-salt a yellow precipitate, which, after washing with cold water, loses but little at 100°, becoming black. It is soluble in aqueous ammonia. Dissolves in boiling water with partial decomposition.

| | | | | | Möller and Strecker. |
|---|---|---|---|---|---|
| 38 C | ...... | 228 | ........ | 53·15 | 54·10 |
| 13 H | ...... | 13 | ........ | 3·03 | 2·99 |
| 10 O | ...... | 80 | ........ | 18·65 | 17·75 |
| Ag | ...... | 108 | ........ | 25·17 | 25·16 |
| $C^{36}AgH^{13}O^{10}$ | ........ | 429 | ........ | 100·00 | 100·00 |

Vulpic acid is easily soluble in *bisulphide of carbon* (Stein). — It dissolves in 200 parts of boiling, and 376 parts of cold *alcohol* of 80 p. c. (Stein); in 588 parts of alcohol of 90 p. c. at 17°, and in 88·3 parts of boiling alcohol. More easily soluble in *ether*, and especially in *chloroform* (Möller & Strecker).

*Addenda to* vol. xiii, p. 8.

# 1. Alphatoluic Acid.

$$C^{16}H^8O^4 = C^{16}H^8,O^4.$$

CANNIZARO. *N. Ann. Chim. Phys.* 45, 468; *Ann. Pharm.* 96, 246; *Chem. Gaz.* 1855, 428; *Lieb. Kopp. Jahresber.* 1855, 622; *Par. Soc. Bull.* 1861, 68; *Ann. Pharm.* 119, 253; *Kopp's Jahresber.* 1861, 421. — *Compt. rend.* 54, 1225; *Ann. Pharm.* 124, 252; *Kopp's Jahresber.* 1862, 267.

MÖLLER & STRECKER. *Ann. Pharm.* 113, 64.

*Formation.* 1. By boiling monochlortoluol $C^{14}H^7Cl^6$ [obtained either

by the action of chlorine on toluol (according to xii, 291) or of hydro-chloric acid on benzyl-alcohol (xii, 18)], with alcohol and cyanide of potassium, cyanide of benzyl, $C^{14}H^7Cy$, is produced. This body, when subjected to prolonged boiling with strong solution of caustic potash, yields alphatoluic acid, with simultaneous evolution of ammonia.

$$C^{16}NH^7 + 4HO = C^{16}H^8O^4 + NH^3 \text{ (Cannizaro)}.$$

2. By boiling vulpic acid (p. 150) with baryta-water (Möller & Strecker).

*Preparation.* Vulpic acid is boiled with hot saturated baryta-water for several hours, or until the solution is completely decolorised, by which methylic alcohol is volatilised, and oxalate of baryta thrown down as a crystalline powder. The excess of baryta is precipitated from the filtrate by carbonic acid; the solution is filtered hot, concentrated by evaporation, and super-saturated with hydrochloric acid; and the crystals which form on cooling are purified by washing with cold water and re-crystallisation.

*Properties.* Colourless, broad, crystalline laminæ, greatly resembling benzoic acid. Melts at 76·5°, solidifying afterwards to a crystalline blistered mass, and volatilises below 100° in irritating vapours. Boils at 265·5° (corrected), and distils unchanged (Möller & Strecker). An acid formed as in (1) was found by Cannizaro to have the same melting-point as that of Möller and Strecker, but a boiling-point of 261—262°. — The solid acid has a sp. gr. of about 1·3. It expands very much on melting, and at 83° has a density = 1·0778, at 135° = 1·0334, that of water at 4° being = 1. The expansion between 83° and 135° amounts to 0·0429 of the volume of the acid at 83°, and consequently to 0·000825 for 1° (Möller & Strecker).

|  |  |  |  |  | Möller and Strecker. |
|---|---|---|---|---|---|
|  |  |  |  |  | *mean.* |
| 16 C | 96 | ........ | 70·59 | ........ | 70·50 |
| 8 H | 8 | ........ | 5·88 | ........ | 5·97 |
| 4 O | 32 | ........ | 23·53 | ........ | 23·53 |
| $C^{16}H^8O^4$ | ........ | 136 | ........ | 100·00 | ........ | 100·00 |

Isomeric with toluic acid (xiii, 8), but belongs to the benzoic series, as is shown by decompositions 2 and 4 (Cannizaro).

*Decompositions.* 1. Dissolves in hot fuming *nitric acid* with transient red colour. The solution deposits, on cooling, colourless needles of nitroalphatoluic acid, which forms yellowish salts with alkalis. — 2. Oxidised by boiling with *sulphuric* acid and *oxide of manganese* or *chromate of potash*, but with difficulty, and only when the acid employed consists of oil of vitriol diluted with not more than an equal weight of water. The products of the oxidation are carbonic acid, formic acid, oil of bitter almonds, and benzoic acid. — 3. Forms with *pentachloride of phosphorus* hydrochloric acid, phosphoric oxychloride, and a colourless, heavy, fuming liquid, *chloride of alphatoluyl*. This last body is converted by aqueous ammonia into *alphatoluylamide*, $C^{16}NH^9O^2$, which is easily soluble in boiling water (Möller and Strecker). — 4. A mixture of the lime-salt and formate of lime yields by distillation an oil, $C^{16}H^8O^2$, which combines with bisulphite of soda to form a crystallisable

compound. The oil is decomposed by distillation, and when heated with nitric acid yields benzoic and nitrobenzoic acids (Cannizaro).

Alphatoluic acid is slightly soluble in cold, easily in boiling *water;* an excess of the acid melts to an oil in the latter.

With *ammonia, alkalis,* and *alkaline earths* it forms easily soluble salts, difficult to crystallise. Sulphate of copper throws down from the ammonia salt a pale-green, amorphous precipitate (Möller & Strecker).

*Silver-salt.* — Precipitated from the ammonia-salt by nitrate of silver. — Delicate, colourless laminæ, which crystallise from a boiling aqueous solution (Möller & Strecker).

|  |  |  |  | Möller and Strecker. |  |
|---|---|---|---|---|---|
| $C^{16}H7O^4$ | ............ | 135 | ........ | 55·56 |  |
| Ag | ............ | 108 | ........ | 44·44 | ........ 44·4 |
| $C^{16}AgH7O^4$ | .... | 243 | ........ | 100·00 |  |

The acid dissolves very easily in *alcohol* and *ether,* and is withdrawn from its aqueous solution by those liquids when shaken therewith.

## 2. Oxatolylic Acid.

$$C^{32}H^{16}O^6 = C^{32}H^{16},O^6.$$
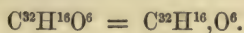
Möller & Strecker. *Ann. Pharm.* 113, 69.

*Formation.* By boiling vulpic acid with caustic potash (p. 150).

*Preparation.* Vulpic acid is boiled with an excess of caustic potash of sp. gr. 1·05 to 1·15 till the precipitate produced by hydrochloric acid in a test-portion of the liquid is no longer yellow, but of a somewhat dirty colour; and the oxatoluic acid formed is precipitated by an excess of hydrochloric acid, and purified crystallisation from alcohol. By prolonged boiling the alkaline liquid becomes paler, though not quite colourless, and gives off methylic alcohol and a little toluol.

*Properties.* Colourless, four-sided, right rhombic prisms, hard and brittle. Melts at 154°. Strongly acid. Does not lose weight at 100°.

|  |  |  |  |  | Möller and Strecker. |
|---|---|---|---|---|---|
|  | *Air-dried.* |  |  |  | *mean.* |
| 32 C | ............... | 192 | ........ | 75·00 | ........ 74·80 |
| 16 H | ............ | 16 | ........ | 6·25 | ........ 6·15 |
| 6 O | ............. | 48 | ........ | 18·75 | ........ 19·05 |
| $C^{32}H^{16}O^6$ | .... | 256 | ........ | 100·00 | ........ 100·00 |

*Decompositions.* 1. Oxatolylic acid *volatilises,* with decomposition, at elevated temperatures, leaving a little charcoal. — 2. Dissolves in fuming *nitric acid* with red colour, which disappears on heating. Water precipitates from the solution a yellow resin, which is resolved into nitrotoluol and oxalic acid by boiling with caustic potash, probably

*nitroxatolylic acid.* — 3. It is resolved, by prolonged boiling with caustic potash of sp. gr. 1·2 to 1·3, into oxalic acid and toluol:

$$C^{32}H^{16}O^6 + 2HO = C^4H^2O^8 + 2C^{14}H^8.$$
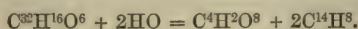
*Combinations.* — The acid dissolves slightly in boiling *water*, and is deposited almost entirely on cooling.

It forms with *alkalis* easily soluble, and with the *alkaline earths* difficultly soluble salts.

*Baryta-salt.* — Obtained as a crystalline precipitate by mixing concentrated solutions of the ammonia-salt and chloride of barium. By re-crystallisation from dilute alcohol it is converted into warts and shining laminæ, which lose 9·9 p. c. of water at 100° (4 at. = 10 p. c. HO).

|          | Dried. |     |        |     | Möller and Strecker. |
|----------|--------|-----|--------|-----|--------|
| 32 C ...................... | 192 | ........ | 59·33 | ........ | 59·25 |
| 15 H ...................... | 15 | ........ | 4·64 | ........ | 4·61 |
| 5 O ...................... | 40 | ........ | 12·36 | ........ | 12·39 |
| BaO ...................... | 76·6 | ........ | 23·67 | ........ | 23·75 |
| $C^{32}H^{15}BaO^6$ .... | 323·6 | ........ | 100·00 | ........ | 100·00 |

*Lead-salt.* — A solution of neutral acetate of lead precipitates from the dilute aqueous ammonia-salt, delicate colourless needles, nearly insoluble in water. — Loses 3·1 p. c. of water at 100°, and a little more at 120°.

|          | At 100°. |     |        |     | Möller and Strecker. |
|----------|--------|-----|--------|-----|--------|
| 32 C ............................ | 192 | ........ | 48·63 | ........ | 48·16 |
| 19 H ............................ | 19 | ........ | 4·81 | ........ | 4·90 |
| 9 O ............................ | 72 | ........ | 18·24 | ........ | 19·49 |
| PbO ............................ | 112 | ........ | 28·32 | ........ | 27·45 |
| $C^{32}PbH^{15}O^6 + 4aq$ .... | 395 | ........ | 100·00 | ........ | 100·00 |

*Silver-salt.* — Crystalline precipitate thrown down from the ammonia-salt by nitrate of silver.

|          | At 100°. |     |        |     | Möller and Strecker. |
|----------|--------|-----|--------|-----|--------|
| 32 C ...................... | 192 | ........ | 52·89 | ........ | 52·87 |
| 15 H ...................... | 15 | ........ | 4·13 | ........ | 4·15 |
| 6 O ...................... | 48 | ........ | 13·22 | ........ | 13·38 |
| Ag ............... | 108 | ........ | 29·76 | ........ | 29·60 |
| $C^{32}AgH^{15}O^6$ .... | 363 | ........ | 100·00 | ........ | 100·00 |

## Oxatolylate of Ethyl.

$$C^{36}H^{20}O^6 = C^4H^5O, C^{32}H^{15}O^5.$$
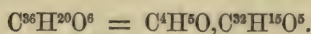
Formed by passing hydrochloric acid gas into the alcoholic acid, or by treating the silver-salt with iodide of ethyl.

Colourless prisms melting at 45·5°. — Insoluble in aqueous ammonia, but easily soluble in alcohol.

|          |     |     |        |     | Möller and Strecker. |
|----------|--------|-----|--------|-----|--------|
| 36 C ............................ | 216 | ........ | 76·06 | ........ | 75·46 |
| 20 H ............................ | 20 | ........ | 7·04 | ........ | 7·00 |
| 6 O ............................ | 48 | ........ | 19·90 | ........ | 17·54 |
| $C^4H^5O, C^{32}H^{15}O^5$ .... | 284 | ........ | 100·00 | ........ | 100·00 |

*Primary Nucleus* $C^{38}H^{24}$; *Oxygen-nucleus* $C^{38}H^{20}O^4$.

# Guaiaconic Acid.

$$C^{38}H^{20}O^{10} = C^{38}H^{20}O^4,O^6.$$
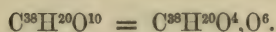
HADELICH. *Dissertation über Bestandth. des Guajakharzes.* Göttingen, 1862; *J. pr. Chem.* 87, 321; *Kopp's Jahresber.* 1862, 466.

Occurs in guaiac-resin to the amount of about 70 per cent.

The alcoholic mother-liquor from which the guaiacic acid has been precipitated by alcoholic potash, in the preparation of guaiacic acid, is evaporated, at 30°, to a thick syrup, and mixed with absolute alcohol, whereby a little of the potash-salt of guaiacic acid is thrown down. This last body is removed; carbonic acid is passed into the filtrate; the liquid, separated from carbonate of potash and mixed with water and a little hydrochloric acid, is heated to drive off the alcohol; and the resin thereby separated is washed with warm water. On cooling, the resin forms a brittle, brown mass, which is resolved, by treatment with ether, into guaiaconic acid soluble in ether, and guaiac beta-resin insoluble in that menstruum. The acid is precipitated from the ethereal solution by caustic potash; the supernatant ether is poured off, and the alkaline solution diluted with water and precipitated with neutral acetate of lead. The green-grey precipitate thus obtained is decomposed under water by hydrosulphuric acid, dried, and exhausted with alcohol, which takes up the guaiaconic acid. It still contains colouring matter, which cannot be entirely removed.

*Properties.* Light-brown, brittle mass, having a conchoïdal fracture, pulverisable to a paler, inodorous, and tasteless powder. Melts between 95° and 100°. Neutral. Rotates a ray of polarised light to the left.

|  | *At* 100° |  |  |  | Hadelich. mean. |
|---|---|---|---|---|---|
| 38 C | 228 | ........ | 69·51 | ........ | 68·95 |
| 20 H | 20 | ........ | 6·09 | ........ | 6·53 |
| 10 O | 80 | ........ | 24·40 | ........ | 24·52 |
| $C^{38}H^{20}O^{10}$ | 328 | ........ | 100·00 | ........ | 100·00 |

Contains also 0·8 p.c. of nitrogen.

Yields an oily distillate when *heated* in a tube. — *Burns* with luminous flame. — Dissolves in *oil of vitriol*, forming a fine cherry-red solution, from which water precipitates violet flocks containing sulphur. — Forms with fuming *nitric acid* a deep orange-yellow solution, which is miscible with water, and yields oxalic acid on boiling. — Coloured a transient blue by *oxidising agents.* — The alcoholic solution reduces *nitrate of silver*.

Insoluble in *water*. The melted acid expels carbonic acid from alkaline carbonates and forms non-crystallisable compounds, which are easily soluble in water and alcohol and decomposible by carbonic acid. — The acetates of baryta, strontia, and lime form pale precipitates with the alcoholic acid.

*Lead-salt.* — The alcoholic acid is precipitated by neutral and basic acetate of lead. The precipitate produced by pouring the acid into excess of neutral acetate contains 37 p. c. of lead; while that produced by adding it to a boiling alcoholic solution of the basic acetate contains 47·26 p. c. of lead.

| | | At 100—130°. | | | Hadelich. mean. |
|---|---|---|---|---|---|
| 38 C | 228 | ........ | 41·37 | ........ | 41·84 |
| 20 H | 20 | ........ | 3·63 | ........ | 3·63 |
| 12 O | 96 | ........ | 17·42 | ........ | 17·48 |
| 2Pb | 207 | ........ | 37·56 | ........ | 37·05 |
| $C^{38}H^{18}Pb^2O^{10},2HO$ .... | 551 | ........ | 100·00 | ........ | 100·00 |

Hadelich regards the fused acid as anhydrous, and the lead-salt, consequently, as $C^{38}H^{20}Pb^2O^{12}$.

Guaiaconic acid is easily soluble in *alcohol, ether, acetate of ethyl, chloroform,* and *acetic acid,* but nearly insoluble in *benzene* and *bisulphide of carbon.*

*Oxyazo-nucleus* $C^{38}NH^{15}O^6$.

# Chelerythrine.

$$C^{38}NH^{17}O^6 = C^{38}NH^{15}O^6,H^2.$$
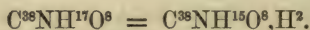
Dana. *Annals of the Lyceum of New York,* 2, 245; *Mag. Pharm.* 23, 125.

Probst. *Ann. Pharm.* 29, 120; 31, 350.

Polex. *N. Br. Arch.* 16, 77.

J. Schiel. *Ann. Pharm.* 43, 233. — *Sill. Am. J.* (2), 20, 220; *J. pr. Chem.* 67, 61; abstr. *N. J. Pharm.* 31, 317: *Lieb. Kopp. Jahresber.* 1855, 566.

Discovered as *Sanguinarine* by Dana in the roots of *Sanguinaria canadensis;* as *Chelerythrine* by Probst, and as *Pyrrhopine* by Polex, in *Chelidonium majus.* Probst & Schiel demonstrated the identity of the two bodies.

*Occurrence.* In *Chelidonium majus* (*Handbuch,* viii [2], 41): more abundantly in the roots and unripe fruit than in the herb, together with chelidonine (Probst; Polex). In the roots of *Glaucium luteum* (*Handbuch,* viii [2], 41), together with glaucopicrine, but not in the herb, which contains glaucine (Probst). — In the roots of *Sanguinaria canadensis* (*Handbuch,* viii [2], 41) [and in the leaves, and doubtless also in the seeds (Gibb)] (Dana), together with one or two other alkaloïds (Probst; Riegel; Wayne). See below.

The roots (and herb collected in autumn) of *Eschholtzia californica* (*Handbuch,* viii [2], 41) contain chelerythrine, or a very similar alkaloid, which may be precipitated from an acetic extract of the plant by ammonia, and extracted from the precipitate by ether. From the ethereal extract it may be thrown down as hydrochlorate, and afterwards purified in the same manner as chelerythrine. It forms a grey-white powder and produces with acids deep-red, neutral, crystallisable salts; from which it is precipitated by ammonia and the alkalis (Walz, *Jahrb. pr. Pharm.* 8, 223).

*Preparation.* From the roots of *Sanguinaria canadensis.* 1. The dried and powdered roots are exhausted with absolute alcohol; the tincture thus obtained is mixed with water, freed from alcohol by distillation, filtered, and precipitated by ammonia; and the grey precipitate is collected and boiled with water and charcoal. After filtering and washing with cold water, the carbonaceous mixture is extracted with alcohol, which leaves the chelerythrine on evaporation (Dana). Or, the hot infusion of the powdered root is precipitated with a little ammonia, potash, or lime, and the precipitate is purified as above. The powdered root may also be digested with water containing hydrochloric or acetic acid; the infusion precipitated with ammonia or potash; and the dark precipitate dissolved in absolute alcohol and mixed with cold water, whereby a white precipitate is formed, which is to be purified with charcoal as before (Dana). — 2. The dried and powdered root is exhausted with ether, and hydrochloric acid gas is passed into the filtrate, when impure hydrochlorate of chelerythrine is thrown down, and is collected and dried. In the ether there remains a brown greasy resin, together with a little chelerythrine, which is recovered by evaporating, exhausting the residue with water containing sulphuric acid, and precipitating with ammonia. — The precipitated hydrochlorate is dissolved in water; the solution is precipitated with ammonia; the precipitate is washed, dried, and dissolved in ether; and the solution is shaken with animal charcoal till the supernatant liquid appears colourless. The precipitate again thrown down from the filtrate by hydrochloric acid gas is decomposed by ammonia-water, and afterwards washed and dried (Probst; Schiel). Schiel purifies chelerythrine extracted by other methods, by precipitating its ethereal solution with hydrochloric acid gas or sulphuric acid.

From the roots of *Chelidonium majus.* 1. The fresh or dried root (or the residue which remains after treatment with aqueous carbonate of soda in the preparation of chelidonic acid, according to xii, 413) is exhausted with water containing sulphuric acid; the liquid is precipitated by ammonia; and the precipitate is washed, freed from water as far as possible by pressing, and dissolved, while still moist, in alcohol containing sulphuric acid. The alcoholic solution, diluted with water, is submitted to distillation, and after the alcohol is driven off, precipitated with ammonia. The precipitate is dried between blotting-paper as quickly as possible, at a very gentle heat, powdered, and treated with ether, which dissolves chiefly chelerythrine. On expelling the ether, there remains a viscid turpentine-like mass, which is to be dissolved in as small a quantity as possible of water containing hydrochloric acid, resin then remaining behind. On evaporating the solution to dryness, and washing the residue with ether, hydrochlorate of chelerythrine remains undissolved. This is dissolved in a little cold water, which leaves most of the hydrochlorate of chelidonine undissolved; the solution is evaporated; and the residue again treated with water so long as hydrochlorate of chelidonine continues to separate. From the last aqueous solution the chelerythrine is thrown down by ammonia, and is purified by washing and drying, and subsequently dissolving in ether and evaporating (Probst). — 2. The dried and coarsely powdered roots, collected in spring, are exhausted by twice boiling with alcohol; water is then added and the alcohol distilled off; and when the residue is perfectly cold, the resin which has separated is removed, and the chelerythrine and chelidonine are thrown down from the filtrate by carbonate of soda.

The washed and dried precipitate treated with boiling alcohol, yields a solution which when filtered, cooled, and concentrated, deposits first chelidonine, and afterwards, on further slow evaporation of the mother-liquor, yellowish warts and black plates of chelerythrine, which is purified by pouring off the mother-liquor at the proper point, picking out the crystals, and re-crystallising from alcohol (Polex).

From *Glaucium luteum*. The dried and powdered roots of plants of one to two year's growth are exhausted with water containing acetic acid; the extract is precipitated by excess of ammonia; and the precipitate is washed, dried, and exhausted with ether, which leaves nearly pure chelerythrine on evaporation. The product is dissolved in the smallest possible quantity of water acidulated with hydrochloric acid; the water and excess of acid are evaporated; and the remaining hydrochlorate of chelerythrine is freed from leaf-green by washing with ether, after which it is dissolved in a little water and mixed with an equal volume of strong hydrochloric acid, which precipitates it almost completely, the supernatant liquid retaining only a small quantity, precipitable by ammonia. The precipitated salt may be obtained in the crystalline form by dissolving it in water and evaporating the solution. By decomposition with ammonia it yields chelerythrine, which is allowed to crystallise from ether, with addition of water (Probst).

With the first year's roots, Probst employs also the following method, which yields *glaucotine* at the same time. The precipitate produced by ammonia in the acetic extract is dissolved in dilute sulphuric acid and again precipitated by ammonia; it is then dissolved in alcohol and ether in succession, and recovered from these solutions, on evaporation, in the form of a turpentine-like mass, which is dissolved in dilute sulphuric acid and mixed with concentrated hydrochloric acid, whereupon the colour of the liquid changes to a dirty brown-red, whilst hydrochlorate of chelerythrine separates.

After separation of the hydrochlorate of chelerythrine by filtration, ammonia throws down from the filtrate a red-blue precipitate, which, after drying, dissolves in absolute alcohol, and remains, on evaporating the solution, as a brittle mass but little soluble in ether. This mass, the *glaucotine* of Probst, is red-blue, soluble in alcohol, but insoluble in ether, and is taken up by acids, with green colour. The neutral hydrochloric acid compound retains the acid when evaporated and further heated, and also dissolves subsequently in water with green colour, but not in ether.

Glaucotine is probably a decomposition-product of chelerythrine (Probst).

*Properties.* Chelerythrine is obtained from absolute alcohol by spontaneous evaporation in groups of crystalline nodules (Probst). White, pearly, fine grains (Dana). Star-shaped groups of transparent needles, and white nodules (Polex). Its ethereal solution leaves, on evaporation, a turpentine-like body, which gradually hardens to a shining friable mass (Probst). The crystals become opaque and brown on drying (Polex). Softens at 65° like a resin (Probst). Tasteless (Schiel); in the mouth it slowly creates a very faint taste (Dana); in alcoholic solution it has a burning sharp taste (Probst); very bitter (Schiel). Acts as a powerful narcotic poison. The dust excites violent sneezing (Probst). According to Dana and Schiel, it has an

alkaline reaction, but according to Probst and Polex, not. — On exposure to the air, it gradually assumes a yellowish-white colour (Dana), and in presence of small quantities of acid vapours becomes immediately red (Polex; Schiel).

|  |  |  |  |  | Schiel. at 100—105°. | | |
|  |  |  |  |  | a. mean. |  | b. |
|---|---|---|---|---|---|---|---|
| 38 C | 228 | ........ | 70·59 | ........ | 69·66 | ........ | 70·34 |
| N | 14 | ........ | 4·33 | ........ | 5·23 | ........ | 5·07 |
| 17 H | 17 | ........ | 5·26 | ........ | 5·16 | ........ | 5·21 |
| 8 O | 64 | ........ | 19·82 | ........ | 19·95 | ........ | 19·38 |
| $C^{38}NH^{17}O^8$ | 323 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

*a* is sanguinarine, *b* chelerythrine. — The above is Limpricht's formula (*Lehrbuch*, 1197). Schiel proposed $C^{38}NH^{16}O^8$; Gorup-Besanez (*Handwörterb.*, 2nd ed. 2, 2, 945), $C^{38}NH^{15}O^5$; Gerhardt (*Traité*, 4, 232), $C^{36}NH^{17}O^8$.

Melts easily when *heated*, and burns completely, with evolution of ammoniacal vapours (Polex). — Is not decomposed by nitric acid.

It is insoluble in *water*.

Chelerythrine unites with *acids*, which it colours a fine orange-red, forming neutral salts, partly crystallisable, having a burning sharp taste, a narcotic action, and dissolving, for the most part, in water. From the solutions, ammonia, alkalis, or magnesia, precipitate chelery-thrine in the form of a grey-white, curdy precipitate (Probst). Concentrated acids have but little action on chelerythrine, in the cold (Polex). Acetate of chelerythrine forms yellowish-white precipitates with tartar emetic, sesquichloride of iron, mercurous nitrate, mercuric chloride, and nitrate of silver. Iodine precipitates the solution of a crimson, chromate of potash of a yellow, and chloride of gold of a dark red-yellow colour. Basic acetate of lead and tincture of galls (see below) do not produce precipitates (Polex).

*Phosphate of Chelerythrine.* — Permanent in the air, and more easily crystallisable than the sulphate. Easily soluble in water and dilute alcohol, difficultly soluble in absolute alcohol, and insoluble in ether (Probst).

*Sulphate of Chelerythrine.* — Obtained by evaporating a solution of chelerythrine in dilute sulphuric acid at a gentle heat, washing the residue with ether, dissolving in alcohol, and allowing the solution to evaporate spontaneously. Crystallises with difficulty. Permanent in the air. Melts to a wax when heated, without decomposition. — Easily soluble in water and dilute alcohol, difficultly soluble in absolute alcohol, insoluble in ether (Probst).

*Hydrochlorate of Chelerythrine.* Red, crystalline, neutral mass, soluble in water and alcohol, but insoluble in ether. Precipitated from the aqueous solution by strong hydrochloric acid (Probst; Schiel).

*Bichloride of Platinum* precipitates the salts of chelerythrine orange-red. Schiel found in the precipitate in his earlier analyses 18·7, 21·7, and 17·7, and afterwards 18·06 p. c. of platinum ($C^{38}NH^{17}O^8$,HCl,PtCl$^2$ requires 18·32 p. c. Pt).

*Acetate of Chelerythrine.* — Easily soluble in water and alcohol, even after evaporation to dryness (Probst). — *Chelidonate of chelerythrine* dissolves in water and alcohol (Probst).

*Tincture of galls* produces in salts of chelerythrine a [yellow-red (Schiel)] precipitate, soluble in alcohol (Probst).

Chelerythrine dissolves very easily in *alcohol*, forming a solution from which it is precipitated by water, and in *ether* (Dana). It is readily soluble in *volatile and fixed oils* (Polex).


*Appendix to Chelerythrine.*

# 1. Glaucopicrine.

PROBST. *Ann. Pharm.* 31, 254.

Occurs in the roots of *Glaucium luteum* (p. 158).

When from an acetic extract of the roots the chelerythrine is precipitated by ammonia, a filtrate is obtained, which, after neutralisation with acetic acid, yields with decoction of oak-bark a precipitate of tannate of glaucopicrine. The washed precipitate is triturated with hydrate of lime and alcohol, and heated; the filtrate is treated with carbonic acid, the alcohol distilled off, and the residue filtered, evaporated, and exhausted with ether. The residue left on evaporating the ethereal solution is separated by treating it with a small quantity of ether into two portions, a purer, which remains undissolved and is subsequently crystallised from hot water, and a less pure, which dissolves and is recovered from the solution by evaporation. The latter portion is dissolved in water containing acetic acid, mixed with basic acetate of lead, and treated with hydrosulphuric acid. The sulphide of lead is separated by filtration, and the glaucopicrine thrown down with it is extracted by oft-repeated boiling with water containing acetic acid. This solution, together with the filtrate from the sulphide of lead, is then saturated with sulphate of soda and precipitated by ammonia. The precipitate is purified, though with difficulty, by dissolving in ether. — The purer portion of the glaucopicrine contains small quantities of a second alkaloïd, precipitated at the same time by tannic acid. This second body forms, with hydrochloric acid, a salt which crystallises in needles and easily deliquesces.


*Properties.* Dazzling white granules, permanent in the air, and of a bitter taste.

Glaucopicrine assumes a dark grass-green colour when heated with excess of *oil of vitriol*, and is converted into a tough green pellicle, which is insoluble in water, acids, and ammonia.

Dissolves in *water*, especially when hot: the concentrated solution becomes covered, on cooling, with a pellicle, which is afterwards precipitated in the crystalline form. — It forms neutral white *salts*, having a bitter, extremely nauseous taste.

*Hydrochlorate of Glaucopicrine.* — Obtained by evaporating a solution of glaucopicrine in hydrochloric acid, washing the residue with ether, and crystallising from water. — Rhombic tables with truncated edges, or tufts of prisms, having a glassy lustre, permanent in the air.

Glaucopicrine dissolves in *alcohol*, and less easily in *ether*. It is withdrawn from its solutions by animal charcoal.

## 2. Glaucine.

Occurs in the herb of *Glaucium luteum*, but not in the root.

The first year's plants are freed from roots and flowers, ground with acetic acid, and pressed. The expressed liquid is heated to precipitate leaf-green, acidified with a little nitric acid, and mixed while still warm with nitrate of lead. After cooling, the fumarate of lead which has separated is collected; the excess of lead is thrown down by hydrosulphuric acid; and the filtrate is neutralised, and precipitated by decoction of oak-bark. This precipitate, when washed and pressed, is triturated in the moist state with hydrate of lime, and the mixture is exhausted with warm alcohol. Carbonic acid is then passed into the alcoholic liquid; the filtrate is evaporated; and the residue washed with a little cold water, which removes colouring matter. The remaining glaucine is crystallised from hot water.

White crusts, made up of small pearly scales. It is deposited from ether as a turpentine-like mass, almost oily at first, but becoming harder on standing. Melts to an oil under water. Tastes bitter and very acrid. Has an alkaline reaction. Turns red in the air, especially in sunshine.

Glaucine is decomposed by *heat*, without subliming. — When heated with *oil of vitriol* till the acid begins to evaporate, it assumes a fine blue-violet colour, without liberation of charcoal or sulphurous acid: on the addition of water, a liquid of a dark cherry-blossom colour is produced, from which ammonia throws down an indigo-blue precipitate. This precipitate dissolves with red colour in acids, and is precipitated unaltered by ammonia; it dissolves in alcohol with blue colour, but is insoluble in water and ether. — *Hydrochloric acid* acts on glaucine in the same manner as oil of vitriol, but less powerfully. *Nitric acid* decomposes it.

Glaucine is soluble in *water*, especially when hot.

It neutralises *acids*, and forms therewith white salts, having a burning acrid taste. It is precipitated from its salts by ammonia in the form of a white curdy precipitate, which speedily cakes together into an elastic mass, and afterwards hardens.

*Phosphate of Glaucine* is not crystallisable.

*Sulphate of Glaucine.* — The dirty-red solution of glaucine in dilute sulphuric acid leaves, on evaporation, shining crystals, which are freed from excess of acid by washing with ether, from red colouring matter by rinsing with absolute alcohol, and further purified by re-crystallisation from alcohol. — Groups of white needles. Dissolves easily in water and absolute alcohol, but not in ether.

*Hydrochlorate of Glaucine.* — A concentrated solution of glaucine in hydrochloric acid solidifies on cooling to a soft mass of fine needles, having a blood-red colour when impure glaucine is used. — White needles and crusts, turning red on exposure to light, and red and dark-blue on spontaneous evaporation of their solution. — The salt dissolves easily in water, but is insoluble in alcohol and ether.

The salts of glaucine are precipitated by *tincture of galls.*

Glaucine dissolves very easily in *alcohol* and *ether*. It is precipitated from its solutions by *animal charcoal*, and is extracted from the charcoal with difficulty by alcohol.

3. *Second alkaloïd of Sanguinaria.* — The name *porphyroxine* given to this body by Gibb (*Pharm. Viertelj.* 10, 56), supposes its identity with the porphyroxine of opium, which, however, is not indicated by the description.

The root is exhausted with water containing acetic acid; the chelerythrine is thrown down by the addition of ammonia; and the filtrate is exactly neutralised with acetic acid, and precipitated with infusion of galls. The precipitate is collected, washed, dried, triturated with hydrate of lime [alcoholic potash (Gibb)], and exhausted with alcohol. The alkaline tincture thus obtained is treated with carbonic acid, the alcohol is distilled off, and the residue evaporated to dryness, and exhausted with boiling water. The aqueous solution is again evaporated, and the residue dissolved in ether. On evaporating the ethereal solution there remains a dirty-white crystalline mass, which is purified by re-crystallisation from alcohol, with the help of animal charcoal.

Small tables, inodorous, tasteless, and very difficultly soluble in water. — Forms with acids colourless, neutral, crystallisable salts, which are bitter and soluble in water. — Dissolves in alcohol and ether (Riegel, *Jahrb. pr. Pharm.* 11, 102).

4. *Third alkaloïd of Sanguinaria. Gibb's Puccine.* —Wayne (*Pharm. Viertelj.* 6, 254) in preparing sanguinarine by the Probst-Schiel method, excepting that he precipitated the ethereal solution with sulphuric acid, found that a second base remained in solution, and was obtained as a dark-red, amorphous residue by evaporating the ether.

This residue was dissolved in ether, again treated with dilute sulphuric acid to precipitate any remaining sanguinarine, then filtered and evaporated to dryness. The residue, when dissolved in alcohol and mixed with water, yielded a precipitate of puccine (or sulphate ? Kr.). This substance, after drying, forms a red, tasteless powder, insoluble in cold water, and melting to a resin in boiling water. An alcoholic solution is rendered pale-yellow by treatment with animal charcoal, and the filtrate leaves on evaporation a pale-red residue, which is coloured dark-red by hydrochloric acid, and afterwards forms bright-red needles. With sulphuric acid red nodules are obtained, a solution of which yields a pale-yellow precipitate with ammonia.

5. *Acrid alkaloïd of Eschholtzia.* — Occurs in the root and herb, together with a bitter alkaloïd, and in autumn accompanied also by chelerythrine. This body is precipitated by ammonia from the extract made with water containing acetic acid, while the bitter alkaloïd remains dissolved in the liquid. The precipitate is to be washed with pure weak ammonia, dried, and dissolved in ether. The colouring matter is removed by evaporating the ethereal solution, dissolving the residue in water containing acetic acid, precipitating with ammonia, &c.; or by digestion with animal charcoal. — White powder, tasteless in itself, but very bitter in alcoholic or ethereal solution. Has an alkaline reaction. Does not assume a violet colour with oil of vitriol. — Insoluble in water, but easily soluble in acids, forming neutral

colourless salts, which are completely precipitated by caustic alkalis and their carbonates in white flocks. The salts are precipitated also by infusion of galls. — The alkaloïd dissolves easily in *alcohol* and *ether* (Walz, *Jahrb. pr. Pharm.* 8, 223 ; *N. Br. Arch.* 42, 133).

6. *Bitter alkaloïd of Eschholtzia.* — After throwing down the chelerythrine and acrid alkaloïd by ammonia from the acetic extract of the plant, the filtrate is neutralised with acetic acid and precipitated by infusion of galls. From this precipitate the bitter alkaloïd is obtained in the same way as the second alkaloïd of sanguinaria from the corresponding precipitate. — Crystalline, easily fusible mass, which has a nauseous, bitter taste, and turns litmus blue. It colours oil of vitriol a fine violet, even on the addition of one drop of a solution containing $\frac{1}{100}$th of the alkaloïd (Walz, *Jahrb. pr. Pharm.* 8, 224).

7. *Colouring matter of the petals of Glaucium luteum* (*Handbuch* viii. [2], 41). — The petals are exhausted with alcohol, acetic acid, and moderately concentrated caustic potash in succession, and the residue is dried and exhausted with ether, which takes up the colouring matter. By evaporating the ethereal solution, washing the residue successively with absolute alcohol, warm caustic potash, and acidulated water, and taking up the colouring matter remaining undissolved by ether, a solution is obtained which, when evaporated, leaves the colour in the form of a deep-yellow, fatty mass. — It melts when heated, and is decomposed at a high temperature. It is bleached by exposure to light. By treatment with strong caustic potash, it appears to yield a substance insoluble in water, but soluble in alcohol ; for after treatment with potash it communicates a yellow colour to absolute alcohol, though not if first washed with acids. — It is precipitated from its ethereal solution by alcohol (Probst, *Ann. Pharm.* 31, 257).

# 8. Chelidoxanthine.

PROBST. *Ann. Pharm.* 29, 128.

In the root, herb, and flowers of *Chelidonium majus* (*Handbuch* viii [2], 41).

The root is first treated with dilute sulphuric acid to remove chelerythrine and chelidonine, as described on page 157; the residue is then exhausted with hot water, and the extract is mixed with neutral acetate of lead, and afterwards treated with hydrosulphuric acid. The precipitated sulphide of lead, after washing with cold water, gives up to boiling water, chelidoxanthine, which is obtained in the form of a friable mass on evaporating the solution. This mass is washed successively with ammonia-water and ether, which remove foreign substances, and the residue is exhausted with absolute alcohol. The solution thus obtained is filtered and evaporated, and the chelidoxanthine which remains is washed with cold dilute sulphuric acid, ammonia-water, and ether. It is lastly dissolved in boiling water, and crystallised by slow evaporation.

Yellow, friable mass, or short yellow needles and crusts. Has a very bitter taste.

Chelidoxanthine dissolves in *oil of vitriol*, with evolution of gas,

forming a yellowish-brown solution, which is not precipitated by water, and only slightly by ammonia.

It dissolves very slightly in cold, but more freely in hot *water*, which it colours a deep yellow. — It is not altered by *acids* or *alkalis*. — Difficultly soluble in *alcohol*; insoluble in *ether*. Precipitated from its aqueous solution by *tincture of galls*.

*Oxyazo-nucleus* C³⁸N³H¹⁵O⁶.

# Chelidonine.

? $C^{38}N^3H^{17}O^6 = C^{38}N^3H^{15}O^6,H^2$.
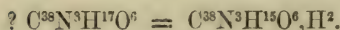
PROBST.    *Ann. Pharm.* 29, 123.
REULING.    *Ann. Pharm.* 29, 131.
POLEX.    *N. Br. Arch.* 16, 77.
WILL.    *Ann. Pharm.* 35, 113.

Observed by Godefroy (*J. Pharm.* 10, 635): obtained pure and investigated by Probst. — Reuling's chelidonine appears to contain chelerythrine.

*Occurrence.* In the root, herb, and unripe seed-capsules of *Chelidonium majus;* most abundantly in the root, together with chelerythrine (p. 156).

*Preparation.* 1. In the preparation of chelerythrine, according to page 157, after precipitating the sulphuric acid extract of the roots with ammonia, and extracting the chelerythrine from the precipitate by ether, there remains a residue which is to be dissolved in the smallest possible quantity of water acidulated with sulphuric acid, and mixed with twice the quantity of strong hydrochloric acid, which throws down hydrochlorate of chelidonine. The salt is decomposed by ammonia-water, and purified by repeatedly dissolving it in a little acidulated water, precipitating with hydrochloric acid, decomposing with ammonia, and lastly by crystallising from boiling alcohol. Or the base may be dissolved in acetic acid and the solution evaporated, when crystals free from acetic acid will be formed. The mother-liquors and wash-waters are precipitated by ammonia, and the precipitate is purified as above (Probst). — 2. The expressed juice of celandine yields, with ammonia, a precipitate containing chelidonine, chelerythrine, a little chelidoxanthine, salts of chelidonic acid, and other substances. The precipitate (which decomposes on standing) is exhausted as quickly as possible with alcohol containing sulphuric acid; the solution is mixed with water; the alcohol distilled off; and the residue, after filtering from the resin which deposits on cooling, is precipitated by ammonia, of which an excess is added to dissolve a brown substance thrown down at first. From this precipitate the chelerythrine is extracted by ether, and the remainder is dissolved in water containing sulphuric acid, and precipitated by strong hydrochloric acid as hydrochlorate of chelidonine. Purification is effected as above (Probst). See the method of Polex (p. 158).

*Properties*. Crystallised chelidonine contains water, which is expelled at 100°. See below. — Inodorous. Tastes acrid, not bitter (Polex); bitter, like sulphate of quinine, and afterwards harsh, probably from impurities (Reuling). Melts at 130° to a colourless oil (Will). Volatilises with aqueous vapour (Reuling). Not poisonous (Probst; Reuling.)

|  |  | at 100° |  |  |  | Will. *mean.* |
|---|---|---|---|---|---|---|
| 38 C | .................... | 228 | ........ | 68·06 | ........ | 67·75 |
| 3 N | ................. | 42 | ........ | 12·54 | ........ | 12·19 |
| 17 H | .................... | 17 | ........ | 5·08 | ........ | 5·62 |
| 6 O | .................... | 48 | ........ | 14·32 | ........ | 14·44 |
| $C^{38}N^3H^{17}O^6$ | .... | 335 | ........ | 100·00 | ........ | 100·00 |

The above is Limpricht's formula (*Lehrb*. 1197). The following formulæ have also been proposed: $C^{40}N^3H^{20}O^6$ (Will); $C^{40}N^3H^{19}O^6$ (Gerhardt); $C^{42}N^3H^{19}O^6$ (Gmelin).

*Decompositions.* 1. Chelidonine when *heated* above its melting point, turns brown, takes fire, and burns with a bright smoky flame. — 2. Submitted to *dry distillation* it yields empyreumatic vapours. — 3. It is decomposed by strong *nitric acid;* when boiled therewith it turns yellow (Polex), dark orange-yellow (Reuling). — 4. Carbonises with hot *oil of vitriol* (Polex). Dissolves in oil of vitriol with carmine-red colour, changing to black (Reuling). — 5. It is not decomposed by *chlorine*, or by aqueous *alkalis* (Reuling). When melted with fragments of caustic potash, it evolves a large quantity of ammonia: if the operation be suspended during the evolution of ammonia, the residue still contains unchanged chelidonine (Will).

*Combinations.* — *With Water*. *Hydrated Chelidonine*. — Colourless tables, having a vitreous lustre (Probst). Transparent tables and cubes (Polex). — Air-dried chelidonine contains 4·89 p. c. of water (2 at. = 5·09 p. c. HO) (Will).

Chelidonine is insoluble in *water* (Probst; Will). A solution prepared with hot water becomes cloudy on cooling, without forming a deposit (Reuling).

The *salts of chelidonine* are colourless when the acid is itself free from colour (Probst; Polex). Reuling obtained orange-coloured salts, probably from his base containing chelerythrine. — They are crystallisable, of an acid reaction, for the most part soluble in water, and have an intensely but pure bitter taste. From solutions of the salts alkalis precipitate chelidonine in the form of a voluminous, curdy precipitate, which becomes granular under the liquid. Solutions of chelidonine-salts containing weak volatile acids lose acid on evaporation (Probst). Acetate of chelidonine yields with tincture of iodine a carmine-coloured, with chromate of potash a yellow, with basic acetate of lead a white, and with solution of gold a dark reddish-yellow precipitate (Polex).

*Phosphate of Chelidonine.* — More easily crystallisable than the sulphate. Fusible, and easily soluble in water and absolute alcohol (Probst).

*Sulphate of Chelidonine.* — Obtained by dissolving chelidonine in dilute sulphuric acid, evaporating, washing away excess of acid by ether, and crystallising from absolute alcohol by spontaneous evapora-

tion of the solution. In warm air the solution dries up to a brittle gum. — Permanent in the air. Melts at 50 to 60° to a viscid mass. Dissolves easily in water and absolute alcohol (Probst).

*Hydrochlorate of Chelidonine.* — Obtained from hot water in delicate crystals. Has an acid reaction and a bitter taste. Dissolves in 325 parts of water at 18°, and is precipitated from the solution by strong hydrochloric acid (Probst).

*Nitrate of Chelidonine.* — Crystals of considerable size, difficultly soluble in water, so that nitric acid throws down a crystalline precipitate from the sulphate and phosphate (Probst).

*Chloroplatinate of Chelidonine.* — Bichloride of platinum throws down from hydrochlorate of chelidonine a yellow flocculent precipitate, afterwards becoming granular. It may be washed with water without decomposition, and is not acted on by boiling nitric acid. Contains 17·42 to 17·6 p. c. of platinum ($C^{38}N^3H^{17}O^6$,HCl,PtCl² requires 18·23 p. c. Pb) (Will).

*Acetate of Chelidonine.* — Obtained by decomposing sulphate of chelidonine with acetate of lead. — The solution of chelidonine in acetic acid [which is obtained with difficulty (Polex)] deposits chelidonine when evaporated by heat. — On spontaneous evaporation the salt dries up to a gum, easily soluble in water and alcohol (Probst).

The salts of chelidonine are precipitated by *tincture of galls*.

Crystallised chelidonine dissolves with difficulty, and only on prolonged boiling, in *alcohol* and *ether* (Polex). The statement of Probst that chelidonine is soluble in alcohol and ether is to be understood only in this sense, as is shown by other statements (Kr.). — Dissolves easily in *volatile* and *fat oils* (Polex, Reuling). — It is precipitated from solutions of its salts by *animal charcoal* (Probst).

*Primary Nucleus $C^{38}H^{26}$; Oxygen-nucleus $C^{38}H^{22}O^4$.*

## Pyroguaiacin.

$$C^{38}H^{22}O^6 = C^{38}H^{22}O^4,O^2.$$
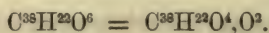
Literature xii., 349; further:
NACHBAUR (& HLASIWETZ). *Wien. Acad. Ber.* 30, 81; *Ann. Pharm.* 106, 382; *J. pr. Chem.* 75, 1; *Kopp's Jahresber.* 1858, 451.
HLASIWETZ & VON GILM. *Ann. Pharm.* 119, 277.

According to Hlasiwetz, the pyroguaiacin obtained by the dry distillation (especially by slow distillation) of guaiacum resin and guaiacic acid is not $C^{14}H^8O^2$, but $C^{38}H^{22}O^6$. (See xiv, 349.)

Pyroguaiacin forms inodorous and tasteless laminæ, which melt at 183°, and solidify in a crystalline mass.

| | Dried at 100° or melted. | | | | Nachbaur. mean. |
|---|---|---|---|---|---|
| 38 C ............... | 228 | ........ | 76·51 | ........ | 76·56 |
| 22 H ............... | 22 | ........ | 7·38 | ........ | 7·37 |
| 6 O ............... | 48 | ........ | 16·11 | ........ | 16·07 |
| $C^{38}H^{22}O^6$ | .... 298 | ........ | 100·00 | ........ | 100·00 |

According to Hlasiwetz it is not a phenyl-compound.

Pyroguaiacin combines with bases. — An alcoholic solution colours *sesquichloride of iron* green. — Does not yield oxalic acid on prolonged boiling with *caustic potash*.

*Potassium-pyroguaiacin.* — A solution of pyroguaiacin in boiling caustic potash forms, on cooling, a semi-solid mass of crystals, which are pressed and dissolved in boiling alcohol. — Fine, delicate prisms and needles, having a satiny lustre. When heated in the air, it assumes first a green, afterwards a blue-green colour. On recrystal- lisation it gives up potash (Hlasiwetz & v. Gilm).

|  |  | Over *oil of vitriol.* |  |  | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|---|
| 38 C | 228 | ........ | 62·81 | ........ | 62·46 |
| 24 H | 24 | ........ | 6·61 | ........ | 6·55 |
| 8 O | 64 | ........ | 17·64 | ........ | 18·85 |
| KO | 47 | ........ | 12·94 | ........ | 12·14 |
| $C^{38}H^{21}KO^6 + 3aq.$ | 363 | ........ | 100·00 | ........ | 100·00 |

Contains, at 100°, 13·89 p. c. KO (by calc. 13·89 p. c. in the anhydrous compound) (Hlasiwetz and v. Gilm).

*Sodium-pyroguaiacin.* — Iridescent laminæ, turning green in warm air. Contains, at 100°, 7·1 p. c. Na, corresponding to the formula $C^{38}H^{21}NaO^6$ (by calc. 7·18 p. c. Na) (Hlasiwetz and v. Gilm).

|  |  | Over *oil of vitriol.* |  |  | Hlasiwetz and v. Gilm. |
|---|---|---|---|---|---|
| 38 C | 228 | ........ | 66·57 | ........ | 66·27 |
| 23·5 H | 23·5 | ........ | 6·86 | ........ | 6·57 |
| Na | 23 | ........ | 6·72 | ........ | 6·85 |
| 8·5 O | 68 | ........ | 19·85 | ........ | 20·31 |
| $C^{38}H^{21}NaO^6 + 2\frac{1}{2}$ aq. | 342·5 | ........ | 100·00 | ........ | 100·00 |

*Oxyazo-nucleus* $C^{38}NH^{19}O^6$.

# Thebaïne.

$$C^{38}NH^{21}O^6 = C^{38}NH^{19}O^6,H^2.$$
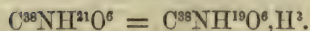
PELLETIER. *J. Pharm.* 21, 565; *N. Br. Arch.* 5, 165; *Schw.* 67, 325; *Ann. Pharm.* 16, 38; abst. *Pogg.* 27, 658. — In opposition to Couerbe: *J. Pharm.* 22, 29.

COUERBE. *Ann. Chim. Phys.* 59, 153; *Ann. Pharm.* 17, 171. — In op- position to Pelletier: *J. Pharm.* 22, 22.

KANE. *Ann. Pharm.* 19, 7.

ANDERSON. *Trans. Roy. Soc. Edin.* 20, 3, 347; *Chem. Soc. Qu. J.* 5, 257; abstr. *Ann. Pharm.* 86, 179; *J. pr. Chem.* 57, 358; *Kopp's Jahresber.* 1852, 537.

*Paramorphine* (Pelletier). — Discovered by Thiboumery in Pelletier's manufactory in 1835.

*Source.* In opium. To the amount of about 1 per cent. (Merck)

Couerbe obtained from 40 pounds of opium about an ounce of thebaïne. — Occurs also in the poppy cultivated in France (Calloud, *N. J. Pharm.* 20, 276).

*Preparation.* In the preparation of morphine by the Couerbe-Mohr process (xvi, 416), when the aqueous extract of opium is precipitated with milk of lime, the morphine remains dissolved in excess of lime, whilst the lime precipitate takes up the thebaïne. The precipitate is washed, dried, and boiled with alcohol; the alcoholic solution is evaporated; and the brown granular mass which remains is treated with ether, which takes up thebaïne, and leaves it on evaporation in the form of a brown, crystalline mass. Purification is effected by dissolving in acids, precipitating with ammonia, and crystallising from alcohol or ether (Pelletier; Couerbe). Anderson obtains thebaïne according to xvi, 420. See Winckler's method (*Repert.* 53, 384).

Mixtures of thebaïne and morphine may be separated by means of ether or weak alcohol, which readily dissolve thebaïne (Pelletier).

*Properties.* White, silvery, quadratic laminæ (Anderson). Needles or small granular crystals, without pearly lustre (Pelletier). Shining, smooth rhomboïdal prisms, crystallising from alcohol in cauliflower-like masses, like grape-sugar (Couerbe). Melts without loss of weight (Kane) at 150° (Pelletier), at 130°, and solidifies again at 110° (Couerbe). Becomes strongly electric when rubbed or powdered. Tastes acrid and styptic rather than bitter. Has an alkaline reaction (Pelletier; Couerbe). Poisonous: one grain given to a dog causes tetanus and death (Magendie).

|  | at 100° | Couerbe. mean. | Pelletier. | Kane. mean. | Anderson. mean. |
|---|---|---|---|---|---|
| 38 C | 228 | 73·31 | 70·99 | 72·09 | 73·23 | 73·08 |
| N | 14 | 4·50 | 6·38 | 4·40 | 6·94 | 4·43 |
| 21 H | 21 | 6·75 | 6·46 | 6·29 | 6·82 | 7·04 |
| 6 O | 48 | 15·44 | 16·17 | 17·22 | 13·01 | 15·45 |
| $C^{35}NH^{21}O^6$ | 311 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

Isomeric with bebirine.

The above is Anderson's formula. Earlier formulæ: $C^{34}NH^{18}O^6$ (Pelletier); $C^{25}NH^{13·5}O^4$ (Couerbe); $C^{25}NH^{14}O^3$ (Kane). — Couerbe's statement, that air-dried thebaïne loses 4 p. c. of water when melted, was not substantiated by Kane's experiments.

*Decompositions.* 1. Thebaïne yields, when *heated*, the ordinary decomposition-products of nitrogenous substances, without volatilising (Pelletier). — 2. It is coloured deep-red by *oil of vitriol*, even when free from nitric acid (Anderson; Winckler). Forms a yellow solution with oil of vitriol (Riegel). Cold sulphuric acid of sp. gr. 1·3 dissolves thebaïne, and deposits on heating a semi-solid resin, probably a product of decomposition, which dissolves in boiling water and separates on cooling in microscopic crystals (Anderson). — 3. Thebaïne is violently attacked by nitric acid, with evolution of red fumes, and forms therewith a yellow solution, which yields a volatile base with caustic potash, assuming a dark colour (Anderson). When digested with strong nitric acid, thebaïne turns soft and yellow, and before dissolving, melts to a soft resin (Pelletier). — *Oil of vitriol* containing *nitric acid* immediately

colours thebaïne red [blood-red (Riegel)], the solution becoming darker on standing: thin layers appear yellowish (Couerbe). The solution in oil of vitriol is coloured first green, afterwards brown, by permanganate of potash (Guy, *Anal. Zeitschr.* 1, 93); it is not altered by peroxide of lead at first, but after 24 hours assumes a faint violet-red colour (Riegel). Chromate of potash produces in the sulphuric acid solution a brisk evolution of gas and a dirty-brown coloration: in the course of 24 hours a white precipitate is deposited, and the liquid becomes colourless (Riegel, *N. Br. Arch.* 58, 287). — 4. *Chlorine* and *bromine* convert thebaïne into a resin (Anderson). — 5. Dry *hydrochloric acid gas* converts it [with evolution of heat (Couerbe, Kane)], into sal-ammoniac and a resinous body, which does not form salts (Liebig, *Ann. Pharm.* 26, 60). Thebaïne is resinised by strong aqueous hydrochloric acid (Pelletier): the solution in dilute acid assumes a dark colour on evaporation, with simultaneous formation of resin, and is no longer completely soluble in water (Anderson). 100 parts of thebaïne absorb 8·35 parts of hydrochloric acid gas (Couerbe); 16·58 parts at 100°, and 17·35 parts more at ordinary temperatures (altogether 33·93 parts) (Kane). — Thebaïne does not colour *ferric salts* blue (Pelletier).

*Combinations.* Thebaïne is very slightly hygroscopic (Kane). — It is insoluble, or nearly so, in *water* (Pelletier; Anderson), and in aqueous *ammonia* and *potash* (Anderson).

Thebaïne dissolves readily in *acids*, forming salts which cannot be crystallised from aqueous solutions, but are easily crystallised from alcohol or ether (Anderson). The salts are precipitated by ammonia and potash (Pelletier), and by the carbonates and bicarbonates of the alkalis, in the case of the last-named reagents even in presence of tartaric acid (Riegel). The precipitates are insoluble in excess of the precipitant.

*Sulphate of Thebaïne.* — Obtained, partly in crystals and partly in the form of a resin, which solidifies to a crystalline mass on standing, by adding sulphuric acid to an ethereal solution of thebaïne (Anderson).

*Hydrochlorate of Thebaïne.* — Thebaïne is mixed with a small quantity of strong alcohol, and alcoholic hydrochloric acid, not in excess, is added till solution is effected: the salt then separates, on standing, in fine rhombic crystals. — Dissolves easily in water and resinises on evaporating the solution. Difficultly soluble in alcohol, especially in absolute alcohol, and insoluble in ether (Anderson).

| | at 100° | | | Anderson. mean. |
|---|---|---|---|---|
| 38 C | 228 | ........ | 62·38 | ........ 62·29 |
| N | 14 | ........ | 3·83 | |
| 24 H | 24 | ........ | 6·56 | ........ 6·71 |
| 8 O | 64 | ........ | 17·52 | |
| Cl | 35·5 | ........ | 9·71 | ........ 10·00 |
| $C^{38}NH^{21}O^6,HCl + 2HO$ .... | 365·5 | ........ | 100·00 | |

*Mercuric chloride* produces with thebaïne a bulky precipitate, and with the hydrochlorate a white crystalline precipitate, neither of which can be obtained of constant composition (Anderson). — *Terchloride of*

*gold* forms with hydrochlorate of thebaïne an orange-yellow precipitate, which melts to a resin at 100° (Anderson).

*Chloroplatinate of Thebaïne.*—Obtained from hydrochlorate of thebaïne and bichloride of platinum. — Yellow crystalline powder, slightly soluble in boiling water, apparently with decomposition (Anderson).

|        |        | at 100° |        |        |        | Anderson. mean. |
|--------|--------|---------|--------|--------|--------|--------|
| 38 C   | ............................................ | 228   | ........ | 42·60 | ........ | 42·56 |
| N      | ............................................ | 42    | ........ | 2·61  |          |       |
| 24 H   | ............................................ | 24    | ........ | 4·48  | .... ... | 4·55  |
| 8 O    | ............................................ | 64    | ........ | 11·98 |          |       |
| 3 Cl   | ............................................ | 106·5 | ........ | 19·89 |          |       |
| Pt     | ............................................ | 98·7  | ........ | 18·44 | ........ | 18·71 |

$C^{38}NH^{21}O^6,HCl,PtCl^2 + 2HO$    ....   563·2   ........   100·00

Thebaïne dissolves easily in *alcohol* [in 10 parts cold (Pelletier)] and *ether*, especially when boiling.

## Bebirine.

$$C^{38}NH^{21}O^6 = C^{38}NH^{19}O^6,H^2.$$
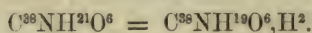
MACLAGAN.   *Ann. Pharm.* 48, 106.
MACLAGAN & TILLEY.   *Ann. Pharm.* 55, 105; *Phil. Mag.* 27, 253; *J. pr. Chem.* 37, 247.
v. PLANTA.   *Ann. Pharm.* 77, 333; *N. Phil. Mag.* 1, 114; *J. pr. Chem.* 52, 287. — *Die Alkaloïde*, Heidelberg, 1846, 26.

Discovered by Rodie in 1834. Occurs in the bark and fruit of the bebeeru or greenheart tree of Guiana, *Nectandra Rodiœi*, Nat. order *Lauraceœ:* See Guibourt (*N. J. Pharm.* 10, 89).

*Preparation. From the bark.* The bark is exhausted by boiling with water containing sulphuric acid; the decoction is concentrated, and filtered from the tannin and sulphate of lime which separate on cooling; and the yellowish-green filtrate is precipitated with ammonia. The dark-grey precipitate thus obtained is washed and dried in the air, whereupon it blackens from containing tannin: it is then dissolved in dilute sulphuric acid and treated with animal charcoal; and the now pale-yellow solution is again precipitated with ammonia, whereby a white precipitate is obtained. This is dried and dissolved in alcohol; the solution is evaporated; and the residue treated with absolute ether, which takes up bebirine and leaves sipeerine undissolved. Both bodies are still to be purified by treating their alcoholic solutions with animal charcoal (Maclagan). Or the grey precipitate produced by ammonia may be freed from tannin by exhausting it with water containing 6 per cent. of caustic potash. The undissolved portion is then to be dissolved in alcohol, and the residue, after evaporation, treated with ether. In this way, however, both bebirine and sipeerine dissolve in the alkaline liquid, from which they may be thrown down in an impure state by sal-ammoniac (Maclagan).

In a later process adopted by Maclagan & Tilley, commercial sulphate of bebirine is decomposed by ammonia, and the precipitate triturated while still moist with freshly precipitated hydrated oxide of lead. This mixture is dried over the water-bath, and the bebirine and sipeerine are extracted by absolute alcohol, and afterwards separated by means of ether. The product obtained in this manner by v. Planta was still impure, as it absorbed oxygen and turned brown on prolonged drying over the water-bath. To purify it, he dissolved it in acetic acid; filtered the solution; added thereto first neutral acetate of lead and then caustic potash; and after completely washing and drying the precipitate of bebirine and oxide of lead, extracted the bebirine by ether. The ethereal solution was evaporated to a syrup and dissolved in alcohol, and on dropping the solution into water, with constant stirring, the bebirine was precipitated as a dense flocculent powder.

*Properties.* White, highly electric powder, permanent in the air (v. Planta). Has a powerful and persistent bitter taste, with a faint resinous after-taste. The alcoholic solution blues litmus strongly (Maclagan). Melts (without loss of weight, after drying at 120°) at 180° to a vitreous mass (v. Planta). Anti-febrile (Maclagan). Resembles caffeine in its physiological effects (*N. Repert.* 11, 521).

|  |  |  |  | Maclagan and Tilley. | | v. Planta. |
|---|---|---|---|---|---|---|
|  |  |  |  | *mean.* |  | *mean.* |
| 38 C ............... | 228 | 73·31 | ........ | 71·46 | ........ | 72·91 |
| N ............... | 14 | 4·50 | ........ | 5·49 | ........ | 4·53 |
| 21 H ............... | 21 | 6·75 | ........ | 6·39 | ........ | 6·89 |
| 6 O ............... | 48 | 15·44 | ........ | 16·66 | ........ | 15·67 |
| $C^{38}NH^{21}O^6$ .... | 311 | 100·00 | ........ | 100·00 | ........ | 100·00 |

The above is v. Planta's formula: Maclagan and Tilley proposed $C^{35}NH^{20}O^6$. — Isomeric with thebaïne.

*Decompositions.* Bebirine decomposes at a temperature above 180°, without subliming (v. Planta). In the *fire* it froths up, evolves strongly-smelling vapours, and leaves a slowly combustible charcoal (Maclagan & Tilley). Aqueous *iodic acid* colours hydrochlorate of bebirine a bright red-brown, changing to dark-red (v. Planta). — Bebirine boiled with dilute *nitric acid* evolves nitric oxide, and is converted into a yellow powder, which dissolves easily in hot, but difficultly in cold water. From a dilute solution of sulphate of bebirine nitric acid throws down the base, for the most part, in its original state (Maclagan, Winckler). — Bebirine forms a black resin with *chromate of potash* and *sulphuric acid.* — Does not yield chinoline when distilled with caustic potash (Maclagan & Tilley).

Bebirine dissolves in 6650 parts of cold, and in 1466 parts of boiling *water* (Maclagan). It is precipitated from its alcoholic solution in a great measure by water (v. Planta).

Bebirine neutralises *acids* completely, and forms therewith un-crystallisable salts. From the hydrochlorate, the base is precipitated by ammonia, the fixed alkalis, and their carbonates and bicarbonates, in white flocks, which dissolve in excess of ammonia or potash somewhat more freely than in excess of the other precipitants. Phosphate of soda throws down white flocks, tincture of iodine a red-brown pre-

cipitate (v. Planta).   Biniodide of potassium precipitates bebirine completely (Wagner).   The salts are all amorphous, and have a very bitter taste, with an accompanying harsh taste (Maclagan).

*Sulphate of Bebirine.* — Pale-yellow, shining.   Soluble in water.

|  |  |  | | Maclagan. |
|---|---|---|---|---|
| C³⁸NH²¹O⁶ | ............................ | 311 | ........  86·38 | ........  86·39 |
| HO | ............................ | 9 | ........    2·50 |  |
| SO³ | ............................ | 40 | ........  11·12 | ........  13·61 |

C³⁸NH²¹O⁶,HO,SO³ ........ ...  360 ........ 100·00

*Hydrochlorate of Bebirine.* — Bebirine absorbs hydrochloric acid gas, without melting, and is converted into a yellow soluble salt, which is left, on evaporating the solution, in transparent scales (Maclagan).

|  |  |  | | Maclagan. |
|---|---|---|---|---|
| C³⁸NH²¹O⁶ | ................. | 311 | ........  89·5 | ........  86·39 |
| HCl | ................. | 36·5 | ........  10·5 | ........  13·61 |

C³⁸NH²¹O⁶,HCl ........ 347·5  ........ 100·0 ........ 100·00

The hydrochlorate forms with *ferric chloride, cupric chloride* and *mercuric chloride,* double salts slightly soluble in hot water and alcohol, from which they separate in a non-crystalline form on cooling (Maclagan & Tilley). Its solution throws down white or yellowish-white amorphous precipitates from *iodide* and *iodomercurate of potassium* (v. Planta ; Delffs). The white precipitate produced by *mercuric chloride* in hydrochlorate of bebirine is converted into a green sticky resin by boiling with water (Hinterberger, *Ann. Pharm.* 82, 319).

The *gold-salt* is yellowish-white and decomposes on exposure to the air (v. Planta).

*Chloroplatinate of Bebirine.* Formed by dropping a strong solution of hydrochlorate of bebirine into dilute chloride of platinum, stirring constantly so that the precipitate may not cake together. — Yellowish-white precipitate, triturable to an orange-yellow powder after drying (v. Planta).

|  |  |  | | Maclagan & Tilley. | v. Planta. mean; *at 120°.* |
|---|---|---|---|---|---|
| 38 C | ............................ | 228 | ........  44·08 | ........  42·42 | ........  44·09 |
| N | ............................ | 14 | ........  2·70 | ......·...  2·53 |  |
| 22 H | ............................ | 22 | ........  4·25 | ........  4·21 | ........  4·66 |
| 6 O | ... ............................ | 48 | ........  9·30 |  |  |
| 3 Cl | ............................ | 106·5 | ........  20·59 |  |  |
| Pt | ............................ | 98·7 | ........  19·08 | ..........  19·12 | ........  18·90 |

C³⁸NH²¹O⁶,HCl,PtCl² .... 517·2  ........ 100·00

Contains 19·2 p. c. of platinum ; but if the same bebirine be dissolved in ether and the solution evaporated in the air, the dark residue yields a platinum-salt containing only 14 p. c. of platinum (Winckler, *N. Repert.* 1, 14).

Hydrochlorate of bebirine precipitates *chloride of iridium and sodium* of an ochre colour; *sulphocyanide of potassium* white; *picric acid* sulphuryellow; it forms precipitates also with *tincture* and *infusion of galls* (v. Planta).

Bebirine dissolves in 5 parts of absolute, and easily in aqueous *alcohol,* and in 13 parts of *ether* (Maclagan).

## Appendix to Bebirine.

1. *Sipeerine.* Preparation, see p. 170. Dark red-brown, shining, non-crystalline, resinous mass, separating from the vessel in which it is prepared in scales. — Very slightly soluble in water. Neutralises acids and forms therewith olive-brown salts. Dissolves easily in absolute and in weak alcohol, but not in ether (Maclagan).

2. *Bebiric acid.* Occurs in the fruit of the bebeeru or greenheart tree. A cold aqueous extract is concentrated and, after cooling, filtered. The bebirine and sipeerine are thrown down by ammonia, and nitrate of baryta is added to the filtrate. The dirty precipitate thus obtained is washed with cold water, dissolved in boiling water, and the solution is evaporated till it crystallises. The crystals, purified by re-crystallisation, are dissolved in boiling water and mixed with neutral acetate of lead; the precipitate thereby produced is washed, and decomposed by hydrosulphuric acid; the filtrate, evaporated to a syrup, is allowed to crystallise over oil of vitriol; and the crystals are purified by dissolving in ether and evaporating the solution in a vacuum.

Deliquescent, white crystalline mass, having a waxy lustre. Melts at 150°, and sublimes undecomposed, in tufts of needles, at a little over 200°. — The potash and soda salts are deliquescent and soluble in alcohol; the lime, baryta, and magnesia salts very slightly soluble in water; the lead-salt but little soluble, even in boiling water (Maclagan).

# 3. Buxine.

FAURÉ. *J. Pharm.* 16, 432; *N. Tr.* 33, 2, 219.
BLEY. *N. Tr.* 25, 2, 64.
WALZ. *N. Jahrb. Pharm.* 12, 302; 14, 15; *Pharm. Virtelj.* 10, 36; abstr. *Chem. Centr.* 1861, 7.

Occurs in the bark and leaves of *Buxus sempervirens.*

*Preparation.* The leaves are boiled with water containing sulphuric acid; the decoction is precipitated by carbonate of soda; and the precipitate thereby formed is washed by decantation, dried, and exhausted with alcohol. The alcoholic solution is evaporated, and the residue is extracted with water slightly acidulated with hydrochloric acid. To this solution is added a large quantity of hydrochloric acid, whereby hydrochlorate of buxine, which is insoluble in strong hydrochloric acid, is thrown down. The precipitate is dissolved in a large quantity of water, again precipitated with carbonate of soda, and the precipitated buxine, dissolved in alcohol, is digested with a mixture of hydrated oxide and basic acetate of lead, by which yellow colouring matter [*buxoflavin* (Walz)] is removed. The oxide of lead dissolved in the filtrate is removed by dilute sulphuric acid; the solution is precipitated by ammonia; and the precipitate, which runs into a resinous mass on warming, is dried, dissolved in ether, and recovered from the solution by evaporation (Walz). — The portion insoluble in ether con-

tains Walz's *buxinic acid.* — Fauré precipitates an aqueous solution of the alcoholic extract of the bark with neutral acetate of lead; frees the filtrate from lead by means of hydrosulphuric acid, and boils with calcined magnesia; and after washing and drying the precipitate, extracts his buxine with alcohol, which leaves it on evaporation in the form of a red mass, triturable to a red-brown powder. By repeated treatment with animal charcoal it may be obtained nearly colourless. Bley adopts a similar process; or, he precipitates a solution of the aqueous extract with basic acetate of lead, decomposes the precipitate under water by hydrosulphuric acid, and boils the washed sulphide of lead with alcohol, which takes up the buxine and leaves it on evaporation as a yellow, crystalline, very deliquescent mass, still contaminated with chloride of calcium (Bley). In this way the greater part of the buxine remains in solution, since it is not precipitated, or only mechanically, by basic acetate of lead (Walz).

*Properties.* Buxine is obtained by the evaporation of its ethereal solution in the form of a coloured resin; when precipitated from its acid solutions by ammonia, or from an alcoholic solution by water, it forms a white powder. It is tasteless at first, but afterwards very bitter. Has an alkaline reaction. Remains unaltered at 180°, but decomposes at higher temperatures (Walz; Fauré).

|        |        |     |        |       |        | Walz.  |
|--------|--------|-----|--------|-------|--------|--------|
| 38 C   | ...... | 228 | ...... | 73·31 | ...... | 72·90  |
| N      | ...... | 14  | ...... | 4·50  | ...... | 4·51   |
| 21 H   | ...... | 21  | ...... | 6·75  | ...... | 6·87   |
| 6 O    | ...... | 48  | ...... | 15·44 | ...... | 15·72  |
| C³⁸NH²¹O⁶.... | | 311 | ...... | 100·00 | ...... | 100·00 |

Isomeric, and according to Walz, identical with bebirine.

Buxine dissolves in 6600 parts of cold, and in 1800 parts of boiling, *water.* — It dissolves in acids, forming neutral non-crystallisable salts, which behave like salts of bebirine with caustic alkalis and their carbonates, with nitric acid, and with all other reagents. The hydrochlorate C³⁸NH²¹O⁶,HCl, forms double salts with mercuric chloride and bichloride of platinum (Walz).

Buxine dissolves in 3 parts of *alcohol* of sp. gr. 0·85, and in 5 parts of absolute alcohol [less freely, therefore? (Kr.)]. It is soluble in 10 parts of commercial, and in 13 parts of absolute *ether* (Walz). According to Fauré it is insoluble in ether.

*Primary Nucleus* C³⁸H³⁰; *Oxygen-nucleus* C³⁹H¹⁴O¹⁶.

## Daphnetin.

$$C^{38}H^{14}O^{18} = C^{33}H^{14}O^{16},O^2.$$
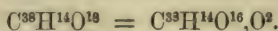
Zwenger. (1860.) *Ann. Pharm.* 115, 1.

*Formation. From Daphnin.* 1. By boiling with dilute sulphuric or hydrochloric acid. — 2. By warming with emulsin. — 3. By contact

with yeast to which a little grape-sugar is added. — 4. By dry distillation. In all cases its production is attended with the formation of sugar or the decomposition-products thereof.

*Preparation.* A. *From Daphnin.* Daphnin is boiled with dilute hydrochloric or sulphuric acid till the liquid becomes yellow. It is then diluted with water, and the crystals which separate on cooling are collected, dissolved in hot water, and precipitated with neutral acetate of lead. The washed precipitate is decomposed under boiling water by hydrosulphuric acid, and the solution filtered. Colourless daphnetin then crystallises out on cooling, and may be purified by re-crystallisation from boiling water. The solution filtered through paper containing iron has a green colour.

B. *From the alcoholic extract of Mezereon bark,* and also from the extract previously exhausted with ether (p. 177). — 1. The extract, mixed with strong hydrochloric acid, is evaporated over the water-bath, and the dry residue is heated more strongly so long as hydrochloric acid is given off, and until it begins to carbonise. The resulting mass is boiled with water; the filtrate is concentrated; and the dark deposit formed on standing is collected and washed with cold water, after which the daphnetin is extracted by boiling water and purified by repeatedly converting it into the lead-salt and decomposing by hydrosulphuric acid. — 2. The alcoholic extract is slowly heated in a half-filled retort, the heat being continued so long as vapours pass over. The crystals which form in the distillate are separated from the liquid portion, and crystallised successively from water and very dilute alcohol, whereby a mixture of daphnetin and umbelliferone is obtained. The crystals dissolved in boiling water, are precipitated by neutral acetate of lead, the liquid is filtered hot, and the precipitated compound of daphnetin with oxide of lead is purified as above. The filtrate, on cooling, yields crystals of umbelliferone.

*Properties.* Delicate, colourless, highly refractive prisms, belonging to the oblique prismatic or monoclinic system. Melts above 250° to a yellowish liquid, which cools to a crystalline solid, and sublimes, even at lower temperatures, especially in a current of air. Has a slightly harsh taste, and when warmed, an agreeable smell, resembling that of coumarin. Its reaction is very slightly acid.

|  |  |  | at 100°. |  |  | Zwenger. mean. |
|---|---|---|---|---|---|---|
| 38 C | ............ | 228 | ........ | 59·06 | ........ | 59·17 |
| 14 H | ............ | 14 | ........ | 3·62 | ........ | 3·81 |
| 18 O | ........ ... | 144 | ........ | 37·32 | ........ | 37·02 |
| $C^{38}H^{14}O^{18}$ | .... | 386 | ........ | 100·00 | ........ | 100·00 |

Contains at 220°, when it begins to sublime, 60·7 p. c. C., or the same proportion as æsculetin (xvi, 23) : it does not, however, resemble the latter body in its behaviour with bisulphites of the alkalis (Rochleder, *Wien. Acad. Ber.* 48, 236).

*Decompositions.* 1. Daphnetin is partially decomposed by *heating* in a closed vessel till it melts. — 2. Dissolves in slightly warmed *oil of vitriol* with yellow colour, and is precipitated by water unchanged; the solution is decomposed by heat. — 3. Colours *nitric acid* dark-red.

— 4. Throws down cuprous oxide from a cold *alkaline solution of cupric oxide,* and rapidly reduces *nitrate of silver.*

*Combinations.* Daphnetin dissolves easily, with yellowish colour, in boiling *water.* — Soluble without alteration in boiling *hydrochloric acid.* — Dissolves in *caustic alkalis* and their *carbonates* with yellow or red-yellow colour, and, when dissolved in water, produces yellow precipitates with *lime-* or *baryta-water.*

*Lead-compound of Daphnetin.* — Aqueous daphnetin forms yellow precipitates with both the neutral and the basic acetate of lead. — A warm aqueous solution of daphnetin is precipitated by aqueous neutral acetate of lead, and the pale yellow precipitate is washed and dried at 100°. — Dark coloured, brittle mass, triturable to a yellow hygroscopic powder. It is partially decomposed by prolonged boiling with water, and then contains 57·60 p. c. of oxide of lead. Dissolves in acetic acid, and colours nitric acid red.

|  | at 100°. |  |  | Zwenger. mean. |
|---|---|---|---|---|
| 38 C | 228 | ........ | 28·61 ........ | 28·17 |
| 10 H | 10 | ........ | 1·25 ........ | 1·38 |
| 14 O | 112 | ........ | 14·07 ........ | 14·46 |
| 4 PbO | 448 | ........ | 56·07 ........ | 55·99 |
| $C^{38}H^{10}Pb^4O^{18}$ | 798 | ........ | 100·00 | ........ 100·00 |

Aqueous daphnetin is coloured green by a small quantity of a *ferric* salt, the colour being destroyed by a larger quantity of the salt, or by the addition of an acid. It is coloured faintly greenish by a very little of a proto-salt of iron.

Daphnetin dissolves easily in boiling *alcohol,* and slightly in *ether.*

*Glucoside of Daphnetin.*

## Daphnin.

$$C^{62}H^{34}O^{38} = C^{38}H^{14}O^{16},2C^{12}H^{10}O^{10}.$$
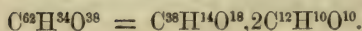
VAUQUELIN. *Ann. Chim.* 84, 174.
C. G. GMELIN & BÄR. *Ueber die Seidelbastrinde.* Tübingen, 1822; *Schw.* 35, 1.
CONST. ZWENGER. *Ann. Pharm.* 115, 1; abstr. *J. pr. Chem.* 82, 196; *Pharm. Viertelj.* 10, 93; *Chem. Centr.* 1860, 823; *Rep. Chim. pure.* 3, 77; *Kopp's Jahresber.* 1860, 552.
ROCHLEDER. *Wien. Acad. Ber.* 48, 236; *Chem. Centr.* 1864, 481; *N. Repert.* 13, 326; *J. pr. Chem.* 90, 442.

Discovered by Vauquelin, and regarded by him and by Gmelin & Bär as a salifiable base, but recognised by Zwenger as a glucoside. — Occurs in the bark of *Daphne alpina* and *D. Mezereum* (*Handbuch,* viii [2], 72), most abundantly at the time of flowering; also in the flowers of the latter plant (Enz, *Pharm. Viertelj.* 8, 25).

The seeds of *Daphne Gnidium* contain Göbel's *coccogninic acid*, which may be obtained by exhausting the alcoholic extract with water. It forms acid, long, 4-sided prisms, and is not precipitated by chloride of barium, lime-water, neutral acetate of lead, or proto sulphate of iron. — Concerning the *acrid principle of mezereon*, see p. 178.

*Preparation.* The alcoholic extract which has been exhausted with ether for the preparation of the officinal *Extractum Mezerei æthereum* may be used instead of the fresh bark.

The alcoholic extract is boiled with water, and the liquid is left for 24 hours to deposit resin. Neutral acetate of lead is then added; the resulting precipitate is removed; and the daphnin is thrown down from the filtrate by basic acetate of lead. This precipitate is decomposed under water by hydrosulphuric acid; the liquid, filtered from sulphide of lead, is evaporated to a syrup, diluted, filtered from resin, again concentrated, &c.; and the syrup is finally freed from resin by repeatedly shaking it with 5 or 6 times its volume of ether. The aqueous liquid separated from the ether quickly solidifies to a mass of crystals of daphnin, which is washed and crystallised from hot water (Rochleder). Zwenger proceeds in a similar manner, but precipitates the daphnin by prolonged boiling with basic acetate of lead: according to Rochleder, however, the liquid filtered from the precipitate produced in the cold yields, on boiling, only a little daphnin, difficult to purify.

*Properties.* Crystallised daphnin (see below) turns opaque below 100°, and loses 8 at. of water at 100°, becoming anhydrous. Anhydrous daphnin melts at about 200° to a colourless liquid, which forms a crystalline solid on cooling (Zwenger).

|  | at 100°. |  |  |  | Zwenger. mean. |
|---|---|---|---|---|---|
| 62 C | 372 | ........ | 52·39 | ........ | 52·42 |
| 34 H | 34 | ........ | 4·78 | ........ | 4·95 |
| 38 O | 304 | ........ | 42·83 | ........ | 42·63 |
| $C^{62}H^{34}O^{38}$ | 710 | ........ | 100·00 | ........ | 100·00 |

Bears a strong resemblance to æsculin (xvi, 22) (Rochleder).

*Decompositions.* 1. Daphnin when *heated* decomposes at a temperature near its melting-point, evolves vapours and a sublimate of daphnetin, and leaves an amorphous residue which becomes coloured when more strongly heated, burns like sugar with access of air, and leaves charcoal if air be excluded (Zwenger). — 2. By boiling with dilute *acids* it is converted into daphnetin and sugar:

$$C^{62}H^{34}O^{38} + 4HO = C^{38}H^{14}O^{18} + 2C^{12}H^{12}O^{12} \text{ (Zwenger)}.$$
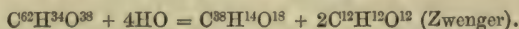
3. *Nitric acid* colours daphnin red in the cold, and converts it into oxalic acid when heated (Gmelin; Zwenger). — 4. A solution of daphnin in caustic *alkalis* or their carbonates, or in lime- or baryta-water, turns brownish-red and decomposes on standing, and more rapidly on boiling (Zwenger). — 5. Daphnin slowly reduces cuprous oxide from a boiling *alkaline solution of cupric oxide.* — 6. It reduces *nitrate of silver* partially only on boiling, but rapidly in the cold, after addition of ammonia (Zwenger). — 7. It is resolved into daphnetin and sugar by warming

with *emulsin,* and partially also by contact with *yeast* and a little grape-sugar (Zwenger).

*Combinations.* — *With Water.* — *Hydrated or Crystallised Daphnin.* Colourless, transparent rectangular prisms, attaining a length of half an inch, or when rapidly crystallised, slender needles (Vauquelin; Zwenger). Tastes extremely bitter (Vauquelin), moderately bitter, afterwards harsh (C. G. Gmelin; Zwenger); Neutral (Zwenger); slightly acid (C. G. Gmelin). — Loses on an average 9·36 p. c. of water at 100° (8 at. = 9·20 p. c. HO), and becomes anhydrous.

|  | | Crystals. | | | | Zwenger. mean. |
|---|---|---|---|---|---|---|
| 62 C | ............................... | 372 | ........ | 47·57 | ........ | 47·17 |
| 42 H | ............................... | 42 | ........ | 5·37 | ........ | 5·57 |
| 46 O | ............................... | 368 | ........ | 47·06 | ........ | 47·26 |
| $C^{62}H^{34}O^{38}$ + 8 aq. | ........ | 782 | ........ | 100·00 | ......... | 100·00 |

Daphnin dissolves very slightly in cold water, but easily in hot water, crystallising from the solution on cooling.

Daphnin dissolves in *caustic alkalis* and their *carbonates* with golden-yellow colour; also in lime- and baryta-water. The latter solutions throw down gelatinous precipitates on boiling. — It is not precipitated by aqueous *neutral acetate of lead* (Vauquelin and others), but is coloured yellow by the *basic acetate* in the cold, and precipitated in combination with oxide of lead on boiling. It is completely withdrawn from its solutions by boiling with *hydrated oxide of lead* (Zwenger). — Colours *sesquichloride of iron* blue, the colour changing to yellow on boiling, while a dark-yellow precipitate is thrown down (Zwenger). Dissolves in cold *alcohol* rather more freely than in water, and very easily in boiling alcohol. — Easily soluble in warm *acetic acid,* from which it crystallises on cooling (Zwenger). According to Vauquelin, it is easily soluble, but according to Zwenger perfectly insoluble, in *ether.*

### Appendix to Daphnin.

*Resin and Acrid Principle of the Daphnads.* — Besides the observations of Landerer given at page 472, vol. xiv, the following have been published.

The alcoholic tincture of the bark of *Daphne alpina* yields on distillation a non-acrid distillate, but on precipitating the resin from the residue by water and distilling the supernatant liquid, an acrid distillate is obtained, while the residue almost entirely loses its harshness. The distillate has an alkaline reaction, and a persistent burning taste: the taste, however, it possesses only after 24 hours. — The precipitated resin is brown and soft, and has a very acrid taste, even when dissolved in alkalis. By treatment with hot water containing sulphuric acid, the acrid principle is removed, and passes over on distilling the acid liquid (Vauquelin, *Ann. Chim.* 84, 186). — Vauquelin afterwards obtained an ammoniacal distillate; also having a persistent acrid taste, either by distilling a decoction of mezereon with alkalis, or by first neutralising the decoction with sulphuric acid, concentrating, and then

distilling with alkalis; or, lastly, by washing the alcoholic extract with hot water, at last containing sulphuric acid, and distilling the liquid with magnesia.

By precipitating an alcoholic extract of the bark of *Daphne Meze-reum*, concentrated and freed from wax, with water, C. G. Gmelin (*Schw.* 35, 11) obtained an acrid resin, the acrid principle of which was not extracted by boiling with hydrochloric acid. On adding alcoholic neutral acetate of lead to an alcoholic solution of the resin, precipi-tating the filtrate therefrom with hydrosulphuric acid, and evaporating the resulting liquid, there remained a thick yellow oil, containing the whole of the acrid principle of the resin. This oil, saponified with caustic potash, yielded a soap which, when distilled with tartaric acid, evolved a powerful odour of phosphoretted hydrogen. — See also Giesse (*Taschenbuch*, 1822, 113), Coldefy-Dorly (*J. Pharm.* 11, 167), Dublanc (*J. Pharm.* 15, 637). — The resinous acid of the bark of *Daphne Mezereum* yields by umbelliferone dry distillation (Zwenger, *Ann. Pharm.* 115, 17).

*Primary Nucleus* $C^{38}H^{35}$.

## Doeglic Acid.

$$C^{38}H^{36}O^4 = C^{38}H^{36}, O^4.$$
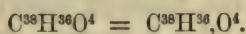
SCHARLING. *J. pr. Chem.* 43, 257; *Lieb. Kopp's Jahresber.* 1847 & 1848, 568.

*Source.* Forms the principal part of doegling train oil.

*Preparation.* The oil is heated to 110—130° with oxide of lead for 10 hours, with frequent additions of a little water, and the plaster thereby formed is boiled with water and afterwards digested with ether; the ethereal solution is filtered; the ether distilled off; and the residual lead-salt decomposed by hydrosulphuric acid.

*Properties.* Yellow-oil, becoming turbid at 16°, and solidifying at a few degrees above 0°. Reddens litmus.

| Dried over chloride of calcium. | | | | Scharling. |
|---|---|---|---|---|
| 38 C | 228 | ........ | 77·03 | ........ | 77·06 |
| 36 H | 36 | ........ | 12·16 | ........ | 12·47 |
| 4 O | 32 | ........ | 10·81 | ........ | 10·47 |
| $C^{38}H^{36}O^4$ | 296 | ........ | 100·00 | ........ | 100·00 |

*Baryta-salt.* — Obtained by neutralising the acid with aqueous am-monia, precipitating with chloride of barium, washing the precipitate without exposure to the air, and crystallising from hot alcohol. Turns yellow and runs together at 100°, without melting.

| at 100° (mean). | | | | Scharling. |
|---|---|---|---|---|
| 38 C | 228 | ........ | 62·74 | ........ | 62·71 |
| 35 H | 35 | ........ | 9·61 | ........ | 9·63 |
| 3 O | 24 | ........ | 6·61 | ........ | 6·46 |
| BaO | 76·5 | ........ | 21·04 | ........ | 21·20 |
| $C^{38}H^{35}BaO^4$ | 363·5 | ........ | 100·00 | ........ | 100·00 |

## Doeglic Ether.

$$C^{42}H^{40}O^2 = C^4H^5O,C^{28}H^{35}O^3.$$
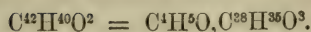
Deposited in the form of a yellow oil on passing hydrochloric acid gas into an alcoholic solution of doeglic acid, and purified by washing with water. Neutral.

|  |  |  |  |  | Scharling. mean. |
|---|---|---|---|---|---|
| 42 C | 252 | ........ | 77·77 | ........ | 77·5 |
| 40 H | 40 | ........ | 12·34 | ........ | 12·7 |
| 4 O | 32 | ........ | 9·89 | ..... ... | 9·8 |
| C$^4$H$^5$O,C$^{58}$H$^{35}$O$^3$ .... | 324 | ........ | 100·00 | ........ | 100·0 |

## Doegling Train Oil.

From the doegling (the *Balæna rostrata* of Chemnitz, *Hyperodon* of later zoologists), a kind of dolphin.

Nearly colourless, or often darker oil, much thinner, and with a less repulsive odour than the other train oils. Sp. gr. 0·8807 at 11°. Becomes turbid at 8°, and semi-solid at 0°, from formation of crystals. Contains, on the average, 78·97 p. c. C., 13·36 H., and 6·77 O., approximating to the formula C$^{62}$H$^{60}$O$^4$, which represents a compound of 1 at. doeglic acid with 1 at. oxide of doeglyl. — Free from iodine and ash-constituents.

When the oil is cooled to 0°, and afterwards filtered, first at 0°, and then repeatedly at increasing temperatures, and the residue is expressed, a solid fat is obtained, amounting to $\frac{1}{48}$th of the oil. This solid fat contains spermaceti, and is partially saponified by potash. The soap, freed from spermaceti, yields a silver-salt containing 42·82 p. c. C., 6·93 H., and 38·90 Ag, corresponding to the formula C$^{20}$H$^{19}$AgO$^4$ (the silver-salt of capric acid).

The oil absorbs oxygen in large quantity, and becomes thicker and specifically heavier. When exposed to the air in a shallow basin, it becomes covered with a pellicle, after the removal of which the remainder dries up only slowly. — By dry distillation it yields a much smaller quantity of acrolein than other fats, and no sebacic acid. When it is rapidly distilled, a gaseous mixture is evolved, containing about 1 vol. of carbonic acid to 6 vols. of hydrocarbons, and a colourless distillate passes over, while a little charcoal and oil remain behind. The distillate is a mixture of various hydrocarbons, volatile acids, and probably undecomposed oil. When it is treated with carbonate of soda and rectified over potassium, at first in the water-bath, the principal product is the hydrocarbon C$^{24}$H$^{24}$ (containing 85·16 C., 14·51 H.: vapour-density = 5·81). The hypothetical combination this hydrocarbon with 1 at. water forms Scharling's *oxide of doeglyl*. — The oil solidifies with nitrous acid.

The oil combines with oxide of lead to form a plaster, from which boiling water extracts, not glycerin, but a small quantity of an acid dark-brown substance. Ether extracts from the plaster the lead-salt of

doeglic acid, and leaves a mixture of lead-salts, the acids of which partly crystallise from alcohol. — Scharling (*Ann. Pharm.* 96, 236) afterwards found in the oil a large quantity of spermaceti, and by saponifying it with potash, obtained doeglal (corresponding to ethal), which solidifies only at temperatures below 0°.

Doegling train-oil dissolves in 2 parts of boiling *alcohol*, and in 22 parts of alcohol at 37°.

### *Primary Nucleus* $C^{38}H^{38}$.

## Fatty Acid $C^{38}H^{38},O^4$.

Obtained in an impure state by Heintz, from cyanide of stethal, $C^{37}C^{37}Cy$, by boiling crude cyanide of cetyl containing that compound with alcoholic potash. See under Margaric acid (xvi, 472).

## COMPOUNDS CONTAINING 40 ATOMS OF CARBON.

### *Primary Nucleus* $C^{40}H^{22}$; *Oxygen-nucleus* $C^{40}H^{12}O^{10}$.

## Euxanthone.

$$C^{40}H^{12}O^{12} = C^{40}H^{12}O^{10},O^2.$$

Stenhouse (1844).   *Phil. Mag.* 25, 322 ; *Ann. Pharm.* 51, 429.
Erdmann.   *J. pr. Chem.* 33, 205 ; 37, 386 ; abstr. *N. J. Pharm.* 10, 154 ; *J. pr. Chem.* 71, 195.
Laurent.   *Compt. chim.* 1849, 377 ; abstr. *Compt. rend.* 26, 33.

*Purrenone.*

*Formation.*   1. By heating euxanthic acid or its salts (Erdmann ; Stenhouse) :

$C^{48}H^{18}O^{22} = 2CO^2 + 6HO + C^{40}H^{12}O^{12}$ (Gerhardt, *N. J. Pharm.* 10, 157).

2. Together with hamathionic acid, by dissolving euxanthic acid in oil of vitriol (Erdmann). — 3. By passing hydrochloric acid gas into alcoholic euxanthic acid, and in small quantities by evaporating euxanthic acid with aqueous hydrochloric acid (Erdmann).

*Preparation.*   1. Euxanthic acid is heated in an air-bath to 160° or 180°, or until it begins to melt, when water and carbonic acid are set free, the decomposition being complete in a few minutes. From the residue warm dilute ammonia-water takes up unchanged euxanthic acid, a brown decomposition-product, and a little euxanthone, which last is deposited again on cooling. The greater part of the euxanthone remains undissolved in the form of a yellow powder, and is purified by

crystallisation from alcohol (Erdmann). — 2. Euxanthone is obtained in fine crystals, though less abundantly than in 1, by heating euxanthic acid in Mohr's sublimation apparatus (Stenhouse). — 3. When a solution of euxanthic acid in oil of vitriol is diluted with a large quantity of water, euxanthone separates in the form of a yellowish-white precipitate, which is washed with water, digested with dilute carbonate of ammonia to remove unchanged euxanthic acid, and crystallised from alcohol (Erdmann).

*Properties.*    Pale-yellow, broad needles or laminæ (Erdmann) ; or, when prepared according to 2, crystals more than an inch long (Stenhouse).   Sublimes undecomposed when carefully heated.   Neutral.

|  |  |  | Stenhouse. mean. |  |  |  | Erdmann. mean. |  | Laurent. |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  | Earlier. | Later. |  |
| 40 C............ | 240 | .... | 68·96 | .... | 68·02 | .... | 68·33 | 68·86 | 68·73 |
| 12 H ........ | 12 | .... | 3·45 | .... | 3·65 | .... | 3·61 | 3·40 | 3·47 |
| 12 O ........ | 96 | .... | 27·59 | .... | 28·33 | .... | 28·06 | 27·74 | 27·80 |
| C⁴⁰H¹²O¹².... | 348 | .... | 100·00 | .... | 100·00 | .... | 100·00 | 100·00 | 100·00 |

Stenhouse examined euxanthone prepared according to 2 ; Erdmann, according to 1, 2, and 3, with similar results. — The above formula, proposed by Gerhardt (*N. J. Pharm.* 10, 157) is now generally adopted, instead of the earlier one of Erdmann and Stenhouse (C¹³H⁴O⁴).

*Decompositions.*    1. Euxanthone *burns* on platinum-foil, without leaving a residue (Stenhouse). — 2. Dissolves in cold *nitric acid* of sp. gr. 1·31, without decomposition at first, but the solution on standing for some time becomes warm, and evolves red vapours, whilst porphyric acid is produced.   When it is heated with nitric acid a violent action takes place, continuing after the removal of the source of heat, with formation of porphyric and oxyporphyric acids, and on boiling, of styphnic and oxalic acids (Erdmann). — 3. Euxanthone does not reduce *alkaline solution of cupric oxide* (W. Schmid, *Ann. Pharm.* 93, 88).

*Combinations.*    Euxanthone dissolves very slightly in *water* (Stenhouse).

It is very little soluble in dilute *acids* (Stenhouse), and nearly insoluble in dilute ammonia, but soluble in strong, warm, aqueous *ammonia*, forming a yellow solution, from which it is deposited unchanged on evaporation (Erdmann).   The ammoniacal solution forms a yellow precipitate with *chloride of magnesium* mixed with sal-ammoniac (Erdmann).   The alcoholic solution does not precipitate *chloride of barium, chloride of calcium, nitrate of silver,* or *neutral acetate of lead,* but throws down a yellow, slimy precipitate from basic acetate of lead (Stenhouse).

Euxanthone is but slightly soluble in *alcohol* or *ether* (Stenhouse).   It dissolves very freely in boiling alcohol, and crystallises from the solution on cooling (Erdmann).

*Appendix to Euxanthone.*

# 1. Porphyric Acid.

ERDMANN. *J. pr. Chem.* 37, 403.

*Dinitro-euxanthone* (Gerhardt).

A solution of euxanthone in cold nitric acid of sp. gr. 1·31, becomes warm on standing, evolves red vapours, and on cooling deposits porphyric acid, which is purified by digesting it with aqueous carbonate of ammonia, washing with water containing carbonate of ammonia, crystallising from pure water, and decomposing with hydrochloric acid.

Yellow crystalline powder, or reddish-yellow, very small crystals. Electric when rubbed.

|  |  |  |  |  | Erdmann. mean. |
|---|---|---|---|---|---|
| 20 C | 120 | ........ | 45·45 | ........ | 43·63 |
| 2 N | 28 | ........ | 10·62 | ........ | 11·82 |
| 4 H | 4 | ........ | 1·51 | ........ | 1·45 |
| 14 O | 112 | ........ | 42·42 | ........ | 43·10 |
| $C^{20}X^2H^4O^6$ | 264 | ........ | 100·00 | ........ | 100·00 |

The above formula was proposed by Gerhardt, who regarded porphyric acid as dinitro-euxanthone (euxanthone = $C^{20}H^6O^6$). Erdmann's formula is $C^{26}X^3H^5O^7$; Laurent's (*Compt. chim.* 1849, 384) contains 1 at. oxygen more.

By boiling with *nitric acid* it yields styphnic (xi, 228) and oxalic acids.

Slightly soluble, with red colour, in *water*; insoluble in acidulated water.

The salts of porphyric acid explode when heated. — The neutral ammonia-salt throws down from chloride of barium, chloride of calcium, neutral acetate of lead, and nitrate of silver, red, for the most part crystalline precipitates, which dissolve in a large quantity of water. — The acid ammonia-salt precipitates from nitrate of silver, pale orange-coloured crystalline scales.

*Ammonia-salt.* — a. *Acid.* — When the salt *b* is kept in a state of fusion at 130°, so long as water and ammonia (amounting to 20·19 p. c.) are given off, the residue dissolves less easily than before in water, and crystallises on cooling in pale-red, feathery crystals, containing 41·41 p. c. C., and 2·16 H.

b. *Neutral.* — Aqueous carbonate of ammonia converts porphyric acid into a blood-red salt, which is insoluble in carbonate of ammonia, but slightly soluble, with yellowish-red colour, in pure water. — On drying it becomes darker, brown-red, and gives off water, and at 130° also ammonia.

|  |  |  |  | Erdmann. mean. |
|---|---|---|---|---|
| 29 C | 120 | ........ | 42·71 | ......... 40·76 |
| 3 N | 42 | ........ | 14·94 | ......... 15·45 |
| 7 H | 7 | ........ | 2·46 | ......... 2·41 |
| 14 O | 112 | ........ | 39·89 | ......... 41·38 |
| $C^{29}X^2H^5(NH^4)O^6$ | 281 | ........ | 100·00 | ......... 100·00 |

*Copper-salt.* — Precipitated on mixing hot solutions of the ammonia-salt and sulphate of copper, in black-red flocks, which become granular on standing, or more quickly when heated. — Microscopic, acute octahedrous.  By boiling with caustic potash, it forms a brown solution and a black precipitate, which is difficult to wash, and explodes when heated.

Porphyric acid is very slightly soluble in cold, but more easily soluble in boiling, *alcohol*.


## 2. Oxyporphyric Acid.

ERDMANN.  *J. pr. Chem.* 37, 407.

Obtained by heating euxanthone with nitric acid till a violent action takes place, and leaving the resulting solution to cool.  The acid which precipitates is dissolved in strong aqueous carbonate of ammonia, to free it from porphyric acid, and precipitated from the filtrate by hydrochloric acid.

Yellow, microscopic crystals, closely resembling porphyric acid.  Does not lose weight at 130°.  Contains, on the average, 42·76 p. c. C., 11·95 N., 1·38 H., and 43·91 O.

According to Erdmann, its formula is $C^{26}X^3H^5O^8$, but according to Laurent it is probably identical with porphyric acid (*Compt. chim.* 1849, 384).

*Nitric acid* converts it into styphnic (xi, 228) and oxalic acids, and at length completely into oxalic acid.

Oxyporphyric acid forms, when digested with carbonate of ammonia, a dark-red salt, remaining on evaporation as a black-red, granular, crystalline mass, which does not turn pale-red when heated (as does the porphyrate of ammonia), and dissolves easily in aqueous carbonate of ammonia.  (Hereby it is distinguished from porphyrate of ammonia.)  The ammonia-salt throws down from salts of the earths and heavy metals red-brown precipitates, which explode when heated, and dissolve in water more easily than those produced by the ammonia-salt of porphyric acid. — Oxyporphyric acid forms a soluble salt with excess of bicarbonate of potash.


*Oxy-chlorine-nucleus* $C^{40}Cl^3H^9O^{10}$.

## Chloreuxanthone.

$$C^{40}Cl^3H^9O^{12} = C^{40}Cl^3H^9O^{10},O^2.$$
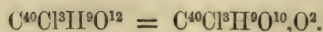
ERDMANN.  *J. pr. Chem.* 37, 397.

From a solution of chloreuxanthic acid in oil of vitriol, water precipitates chloreuxanthone as a yellow powder, which crystallises from alcohol in yellow, feathery crystals.

|  | Crystals. |  |  |  | Erdmann. |
|---|---|---|---|---|---|
| 40 C ..................... | 240·0 | ........ | 53·15 | ........ | 52·28 |
| 3 Cl ........ ............ | 106·5 | ........ | 23·59 | ........ | 23·30 |
| 9 H ..................... | 9·0 | ........ | 1·99 | ........ | 2·14 |
| 12 O ..................... | 96·0 | ........ | 21·27 | .... ... | 22·28 |
| $C^{40}Cl^3H^9O^{12}$ ........ | 451·5 | ........ | 100·00 | ........ | 100·00 |

Primary Nucleus $C^{40}H^{24}$; Oxy-azo-nucleus $C^{40}NH^{15}O^8$.

## Berberine.

$$C^{40}NH^{17}O^8 = C^{40}NH^{15}O^8,H^2.$$
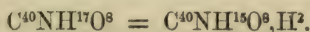
CHEVALLIER & PELLETAN. J. Chim. méd. 2, 314; Berz. Jahresb. 7, 266.

J. A. & L. A. BUCHNER. Repert. 52, 1; Ann. Pharm. 24, 228; Berz. Jahresb. 16, 228; Repert. 56, 177.

G. POLEX. N. Br. Arch. 6, 264.

G. KEMP. Repert. 73, 118; Chem. Gaz. 1847, 209; Lieb. Kopp's Jahresb. 1848 and 1849, 636.

HERBERGER. Jahrb. pr. Pharm. 4, 82.

FLEITMANN. Ann. Pharm. 59, 160.

SCHAFFNER. Jahrb. pr. Pharm. 12, 281.

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Discovered as Xanthopicrite, in 1826, by Chevallier and Pelletan, in the bark of Xanthoxylum Clava Herculis, L., and as berberine in 1835, by

L. A. Buchner in *Berberis vulgaris*, Buchner & Herberger (*Repert.* 36, 1) and Brandes (*Br. Arch.* 11, 29) having previously described a yellow bitter principle, a colouring matter, and a resin from barberry root. Berberine was first investigated more fully by Fleitmann, who showed that the body obtained by Buchner's process, was the hydrochlorate and not pure berberine. Kemp recognised berberine as a vegetable base in 1841. Perrins, in 1862, showed the identity of xanthopicrite with berberine. Perrins and Hlasiwetz & v. Gilm corrected Fleitmann's formula.

Berberine occurs also in the following plants and organs of plants : —in the flowers of the barberry (Ferrein, *Pharm. Viertelj.* 7, 257) ; in Indian varieties of barberry (Solly) ; in the columbo root of *Cocculus palmatus* (*Menispermeæ*), (Bödeker) ; in the bark of *Cæloelyne polycarpa* (*Anonaceæ*) from Abecouta in Western Africa (Stenhouse) ; in the wood *of Coscinium fenestratum* (*Menispermeæ*), from Ceylon (Perrins) ; in *Xanthorriza apiifolia* (Perrins) and *Hydrastis canadensis* (Mahla), two American *Ranunculaceæ*.

The following also contain berberine :—A yellow dye-wood from Upper Assam, the *Woodunpar* of the natives ; the wood of St. John's root from the Rio Grande ; the yellow bark of the *Pachnelo* tree of Bogota ; the root of *Coptis Tecta* or *Mahmira*, an Indian and Chinese species of ranunculus.

The *Papaveraceæ*, *Leontice thalichroïdes*, *Jeffersonia diphylla*, and *Podophyllum pellatum* contain berberine: the *podophyllin* (*Pharm. Viertelj.* 9, 121) prepared from the last named plant, is a mixture of resin and berberine (F. F. Mayer, *Pharm. Viertelj,* 13, 108).

The berberine in barberry root is not perceptible under the microscope ; but when a thin slice of the root is moistened with alcohol and afterwards with nitric acid, crystals of nitrate of berberine form in the vessels, which are thus shown to be the parts in which the berberine occurs (*Apoth. Zeit.* 1863, 27). — The wood of a Mexican variety of barberry contains berberine in the form of a golden-yellow powder deposited in the cracks (Wittstein, *Repert.* 86, 258).

Concerning *barberry-orange*, see Herberger (*Jahrb. pr. Pharm.* 4, 82). — On the identity of jamaicine and berberine see under *Jamaïcine* (Appendix to *Quinine*).

*Preparation.* 1. *From the bark of Barberry-root.* The comminuted bark is exhausted with boiling water, and the liquid is evaporated to a soft extract, which is treated with boiling alcohol so long as it imparts thereto a bitter taste. The tincture, freed from the greater part of the alcohol by distillation, deposits on standing for twenty-four hours in the cold, delicate yellow crystals, which are separated from the mother-liquor by pressing, and purified by washing with cold water and crystallising from boiling water or alcohol (Buchner).

The crystals thus obtained are not pure, but consist partly or wholly of hydrochlorate of berberine. Fleitmann, therefore, converts them into sulphate by means of dilute sulphuric acid ; dissolves the salt in water ; adds baryta-water to alkaline reaction ; and passes carbonic acid into the liquid. After evaporation, the berberine is extracted by alcohol ; the alcoholic solution is precipitated by ether ; and the precipitate is crystallised from water. The nitrate of berberine obtained by other modes of preparation may be decomposed in a similar manner.

2. *From the roots of Hydrastis canadensis.* — The powdered root is

exhausted with hot alcohol in a percolator; the tincture is evaporated; the residue is mixed with water, filtered, and precipitated by hydrochloric acid; and the precipitated hydrochlorate of berberine is purified by crystallisation from boiling alcohol (Mahla). Or, the root is exhausted with boiling water and the liquid evaporated to an extract, which is digested with boiling alcohol. The alcoholic solution is distilled, and to the residue a little dilute nitric acid is added, when, on standing for a day or two, nitrate of berberine crystallises out, and may be freed from resin by repeated crystallisation from water containing nitric acid, with the help of a little animal charcoal (Perrins). *Hydrastis canadensis* yields 4 p. c. of crude berberine (Perrins).

3. *From Columbo root.* An alcoholic extract of the root is exhausted with hot lime-water, and the brown-red solution thus obtained is filtered and neutralised with hydrochloric acid, whereby an amorphous precipitate is thrown down. The filtrate, to which an excess of hydrochloric acid is added, throws down, on standing for two days, a crystalline deposit of hydrochlorate of berberine, which is dissolved in alcohol of 85 p. c., precipitated from the solution by ether, and washed with ether on a filter (Bödeker).

*Properties.* The anhydrous (? Kr.) crystals obtained by drying at 100° (see *Hydrated Berberine*, p. 189) melt at 120° to a red-brown resin (Fleitmann). Neutral towards vegetable colours. Without action on polarised light (Henry). Not poisonous. Tastes bitter (Buchner).

| | | | | Fleitmann. *mean.* at 100°. | | Henry. *mean.* at 120—140°. |
|---|---|---|---|---|---|---|
| 40 C ............... | 240 | ....... | 71·64 | ........ | 67·01 | ........ 69·50 |
| 14 N ............... | 14 | ....... | 4·18 | | | |
| 17 H ............... | 17 | ....... | 5·08 | ........ | 5·68 | ........ 5·32 |
| 8 O ............... | 64 | ....... | 19·10 | | | |
| $C^{40}NH^{17}O^8$ .... | 335 | ........ | 100·00 | | | |

Buchner's analysis (*Repert.* 52, 17) refers only to hydrochlorate of berberine. According to Fleitmann, the formula at 100° is $C^{42}NH^{18}O^9 + 2HO$; according to Kemp $C^{42}NH^{17}O7$; according to Henry (who adopted Gerhardt's supposition) $C^{42}NH^{19}O^{10}$; according to Stas (*Inst.* 1859, 462) $C^{44}NH^{19}O^{10}$. The above formula was shown to be correct by Perrins, from analyses of the salts, and by Hlasiwetz, from analysis of hydroberberine.

*Decompositions.* 1. Berberine *heated* to 160°—200° evolves yellow vapours which condense to an oil, and leaves a difficultly combustible charcoal (Fleitmann). This yellow body is produced also by the dry distillation of chromate of berberine; it dissolves in alcohol and is precipitated of a yellow colour by neutral acetate of lead and by water. It reduces nitrate of silver (Fleitmann). — 2. *Sodium-amalgam* decolorises boiling solution of berberine, with separation of yellow hydroberberine (Hlasiwetz). — 3. When heated to 190°—200° with *water* in a sealed tube, for several days, it becomes uncrystallisable and dark-brown, and on slow evaporation deposits on the sides of the vessels a mass, which has a red colour and bronze-like lustre by transmitted light, and a green colour by reflected light. This mass is but slightly soluble in cold water, but dissolves in acids with fine purple colour, which is changed to green by alkalis. Its alcoholic solution is dichroic, red and green (Hlasiwetz).

4. Hydrochlorate of berberine is not altered by trituration with *bromine* (Buchner). Bromine added to the extent of 2 at. to aqueous berberine or the hydrochlorate, colours the solution dark-red and throws down a dirty-yellow precipitate, a solution of which in boiling alcohol yields crystals of hydrobromate of berberine. A black resin precipitable by ammonia, is also produced (Henry). — 5. In an atmosphere of dry *chlorine*, berberine assumes a blood-red colour, and becomes easily soluble in water; chlorine passed into this solution turns it of a pale-brown colour and throws down brown flocks, which dissolve in caustic potash and are precipitated by acids (Buchner). According to Polex, chlorine colours aqueous hydrochlorate of berberine a fine purple-red; according to Schaffner, it throws down a brown precipitate, whilst the alcoholic solution is only rendered darker in colour. (See also Henry). *Chloride of lime* decomposes berberine (Chevallier & Pelletan).

6. Strong *nitric acid* dissolves hydrochlorate of berberine, forming a dark-red liquid, from which ammonia precipitates brown flocks; on continued heating, the solution becomes clearer, evolving at the same time nitric oxide gas, and after evaporating to a syrup and diluting with water, deposits a yellow, difficultly soluble wax (Fleitmann). Buchner obtained only oxalic acid; Henry obtained oxalic acid, resin, and small crystalline nodules. — 7. Hydrochlorate of berberine dissolves in *oil of vitriol*, forming an olive-green (Buchner), a greenish-yellow (Mahla), a red-brown (Chevallier & Pelletan), a violet-red solution (Polex). These differences may perhaps be caused by the presence of nitric oxide (Kr.). The olive-green solution is decolorised by dilution with water, depositing brown flocks of humus (Buchner). Prolonged boiling with dilute sulphuric acid renders berberine partly uncrystallisable (Chevallier & Pelletan).

8. *Hydrosulphate of ammonia* saturated with sulphur throws down from hydrochlorate of berberine a brown-red precipitate, having a repulsive odour of mercaptan, and containing, after washing, 16·53 p. c. of sulphur. When treated with hydrochloric acid, it does not evolve hydrosulphuric acid or other gas, but becomes paler, and deposits yellowish-red crystals, a solution of which, as well as that of the precipitate, yields a fine red precipitate with neutral acetate of lead (Fleitmann).

9. Berberine is not decomposed by a day's boiling with strong alcoholic *potash*, or by heating therewith in a sealed tube; but if it be evaporated with caustic potash and a little water till the melting mass froths up and gives off hydrogen, together with an odour of chinoline, the mass, supersaturated with sulphuric acid, throws down a large quantity of a dirty-brown humus, whilst an acid, C¹⁶H⁸O⁸, resembling protocatechuic acid, soluble in ether, and a second acid insoluble in ether, remain in solution (Hlasiwetz & v. Gilm). — 10. By distilling berberine with *milk of lime* or *oxide of lead*, chinoline is obtained (Bödeker).

11. Berberine heated with *iodide of ethyl* is converted, according to Perrins, into hydriodate of berberine, but, according to Henry, into iodide of ethylberberine. Henry obtained pale-yellow needles,

slightly soluble in alcohol and cold water, and more freely soluble in hot water, containing 52·66 to 53·48 p. c. C., and 4·70 to 4·91, $C^{40}NH^{16}(C^4H^5)O^8,H^9 = 53·76$ p. c. C., 4·81 H. When heated with *iodide of amyl*, it yields hydriodate of berberine (Henry).

*Combinations. With Water.* — *Hydrated or Crystallised Berberine.* Delicate yellow needles, which give off 19·26 p. c. of water at 100° (Fleitmann).

|  | Crystals. |  |  | Fleitmann. |
|---|---|---|---|---|
| $C^{40}NH^{17}O^8$ ..................... | 335 | ........ | 80·53 | |
| 9 HO ..................... | 81 | ........ | 19·47 | ........ 19·26 |
| $C^{40}NH^{17}O^8$ + 9 aq. ?.... | 416 | ........ | 100·00 | |

Berberine dissolves with difficulty in water (Chevallier & Pelletan). It easily forms supersaturated solutions.

*With Ammonia?* — Hydrochlorate of berberine dissolves in warm aqueous ammonia, forming a dark-brown liquid, which deposits brown crystals on cooling. After washing and drying, the crystals evolve with aqueous potash a large quantity of ammonia (Schaffner). According to Buchner also, berberine combines with ammonia.

Dilute solution of caustic potash throws down berberine from its [aqueous? (Kr.)] solution in conglomerated masses (Fleitmann). Solutions of pure berberine are not coloured red by alkalis (Perrins).

With *acids* berberine forms crystallisable salts (Kemp; Fleitmann). The salts are for the most part *mon-acid*, and more easily soluble in pure water than in acid or saline solutions. Mineral acids and glacial phosphoric acid throw down crystals from aqueous hydrochlorate of berberine. Acetic, tartaric, racemic, citric, and oxalic acids dissolve hydrochlorate of berberine in the same manner as water (Buchner). The salts are generally golden-yellow, neutral and bitter (Kemp). They are obtained pure only by repeated crystallisation till the mother-liquor is no longer deepened in colour by ammonia (Perrins). Ammonia decomposes the salts incompletely (Fleitmann). Caustic potash throws down berberine, which cakes together to a brown resin on boiling (Buchner; Mahla).

Hydrochlorate of berberine forms yellow double salts, crystallising in needles, with the chlorides of magnesium, zinc, cadmium, and uranium, and with sesquichloride of iron, bichloride of tin, and terchloride of antimony (Henry). It precipitates [by forming double-salts, or on account of the difficult solubility of hydrochlorate of berberine in saline solutions? (Kr.)] chloride of manganese, proto- and bichloride of tin, nitrate of cobalt, and tartar emetic, yellow ; the sulphates of copper and nickel, yellowish-green ; sesquichloride of iron and nitrate of bismuth, orange. It does not form precipitates with the sulphates of iron and zinc, or with neutral or basic acetate of lead (Buchner).

*Sulphate of Berberine.* — *Bi-acid.* — The reddish-yellow solution of hydrochlorate of berberine turns pale-yellow on addition of dilute sulphuric acid, and after standing for some time deposits delicate, pale

reddish-yellow needles, which do not lose weight by drying in a vacuum at 100° (Fleitmann).

| | | at 100°. | | | Fleitmann. mean. |
|---|---|---|---|---|---|
| 40 C | .............................. | 240 | ........ | 55·42 | ...... 55·40 |
| N | ........ ..................... | 14 | ........ | 3·23 | |
| 19 H | ......... ................ .... | 19 | ........ | 4·39 | ........ 4·60 |
| 10 O | .............................. | 80 | ........ | 18·48 | |
| 2 SO³ | .............................. | 80 | ........ | 18·48 | ........ 17·99 |
| C⁴⁰NH¹⁷O⁸,2(HO,SO³) .... | | 433 | ........ | 100·00 | |

*Hydriodate of Berberine.* — Formed by dissolving berberine in hydriodic acid (Henry), or by precipitating a weak solution of nitrate of berberine in hot dilute alcohol with iodide of potassium (Perrins). — Small yellow (Perrins) or reddish-yellow needles, soluble in 2130 parts of cold water, more easily in boiling water, and insoluble in alcohol (Henry). Does not undergo any alteration at 100° (Perrins).

| | | at 100—120°. | | | Henry. | | Perrins. mean. |
|---|---|---|---|---|---|---|---|
| 40 C | .. ................. | 240 | ........ | 51·83 | ........ 51·59 | ........ | 51·75 |
| N | ..................... | 14 | ........ | 3·03 | | | |
| 18 H | ..................... | 18 | ........ | 3·88 | ........ 4·23 | ........ | 3·94 |
| 8 O | ..................... | 64 | ........ | 13·83 | | | |
| I | ..................... | 127 | ........ | 27·43 | ........ 25·71 | ........ | 27·07 |
| C⁴⁰NH¹⁷O⁸,HI .. | | 463 | ........ | 100·00 | | | |

*Iodo-hydriodate of Berberine.* — A. When iodine in slight excess is added to aqueous or alcoholic solutions of berberine-salts, red-brown prisms are produced, which after drying over oil of vitriol do not lose weight at 100°. These crystals are very slightly soluble in cold water or alcohol : nitrate of silver precipitates from their solutions the whole of the iodine, forming nitrate of berberine. — B. Besides crystals of hydriodate of berberine and the red crystals just mentioned, shining green spangles are obtained on adding dilute biniodide of potassium, not in excess, to a hot alcoholic solution of a berberine-salt. The same green spangles but of larger size, are formed from hydriodate of berberine, when this salt has been prepared by heating alcoholic berberine with iodide of ethyl to 100°, and afterwards exposing the tube containing the mixture to sunshine for an hour or two, or to diffused daylight for some days. When thus formed, it passes on longer exposure to sunshine into the red salt.—Black-green, rhombic prisms and laminæ, having a metallic lustre : when very thin, they transmit light of a red-brown colour and polarise it completely ; thicker crystals are perfectly opaque. The green crystals are easily converted into red, and *vice versâ.* Permanent at 100° (Perrins).

| | | | | | Perrins. | | |
|---|---|---|---|---|---|---|---|
| | | | | | A. | | B. |
| 40 C | ..................... | 240 | ........ | 33·47 | ........ 33·49 | ........ | 35·65 |
| N | ..................... | 14 | ........ | 1·95 | | | |
| 18 H | ..................... | 18 | ........ | 2·51 | ........ 2·58 | ........ | 2·78 |
| 8 O | ................. ....... | 64 | ........ | 8·93 | | | |
| 3 I | ..................... | 381 | ........ | 53·14 | ........ 53·36 | | |
| C⁴⁰NH¹⁷O⁸,I²,HI .... | | 717 | ........ | 100·00 | | | |

The above is the formula given by Perrins. B contained hydriodate of berberine, which cannot be separated.

*Hydrobromate of Berberine.* — Formed by dissolving berberine in hydrobromic acid (Henry), or thrown down as a yellow precipitate by adding bromide of potassium to a mixture of nitrate of berberine and acetic acid (Perrins). — Delicate, fawn-coloured needles, which, after drying in a vacuum, lose 5·75 p. c. of water at 100° (3 at. = 6·07 p. c. HO.), and assume a bright orange colour (Perrins). Easily soluble in water and alcohol (Henry); insoluble in aqueous bromide of potassium (Perrins).

| | | at 100°. | | | | Henry. | | Perrins. mean. |
|---|---|---|---|---|---|---|---|---|
| 40 C | ......... | 240 | ...... | 57·69 | ...... | 56 87 | ...... | 57·61 |
| N | ......... | 14 | ...... | 3·37 | | | | |
| 18 H | ......... | 18 | ...... | 4·32 | ...... | 4·78 | ...... | 4·34 |
| 8 O | ......... | 64 | ...... | 15·39 | | | | |
| Br | ......... | 80 | ...... | 19·23 | ...... | 18·16 | ...... | 19·00 |
| $C^{40}NH^{17}O^8,HBr$ | .... | 416 | ...... | 100·00 | | | | |

*Hydrochlorate of Berberine.* — Preparation, see above. 100 parts of berberine take up 11·07 parts of hydrochloric acid gas (1 at. = 10·9 parts) (Schaffner). Shining, bright-yellow, loose, inodorous powder, consisting of microscopic crystals (Buchner; Mahla). Long, delicate, golden needles, having a silky lustre (Perrins). Neutral. Has a pure, intensely bitter taste, which is very persistent (Buchner). Gives off 8·65 of water at 100° (4 at. = 8·33 p. c. HO.) (Fleitmann), decomposing slightly, so that it afterwards forms a red solution with water (Perrins). The dried salt is very hygroscopic. — It dissolves with difficulty in cold water and alcohol, but colours both liquids deep-yellow, and dissolves in all proportions in the boiling liquids. Insoluble in ether and bisulphide of carbon (Buchner; Mahla).

| | | at 100--110° | Buchner. | Fleitmann. | Bödeker. | Perrins. | Mahla. |
|---|---|---|---|---|---|---|---|
| 40 C | ... ......... | 240 .... | 64·60 .... | 60·40 .... | 62·65 .... | 62·71 .... 62·79 .... | 64·77 |
| N | ......... | 14 .... | 3·76 .... | 4·03 .... | 3·60 | 3·78 .... | 3·56 |
| 18 H | ......... | 18 .... | 4·84 .... | 5·49 .... | 5·55 .... | 5·07 .... 5·67 .... | 5·14 |
| 8 O | ......... | 64 .... | 17·24 | | 19·31 | 18·74 .... | 17·95 |
| Cl | ......... | 35·5 .... | 9·56 | | 8·89 .... | 9·06 .... 9·02 .... | 8·58 |
| $C^{40}NH^{17}O^8,HCl$ | .... | 371·5 .... | 100·00 | | 100·00 | 100·00 .... | 100·00 |

*Chlorate of Berberine.* — Chlorate of potash throws down from aqueous hydrochlorate of berberine, a yellow bulky precipitate, which is to be washed with water and crystallised from alcohol. — Greenish-yellow crystals, which explode by friction or percussion. Soluble in water; difficultly soluble in aqueous chloride of potassium or chlorate of potash (Fleitmann).

| | | | | | | Fleitmann. |
|---|---|---|---|---|---|---|
| 40 C | ......... | 240 | ...... | 57·21 | ...... | 57·02 |
| N | ......... | 14 | ...... | 3·33 | | |
| 18 H | ......... | 18 | ...... | 4·29 | ...... | 4·29 |
| 14 O | ......... | 112 | ...... | 26·69 | | |
| Cl | ......... | 35·5 | ...... | 8·48 | | |
| $C^{40}NH^{17}O^8,HO,ClO^5$ | .... | 419·5 | ...... | 100·00 | | |

*Nitrate of Berberine.* — Preparation (p. 187). Or hydrochlorate of berberine is decomposed by nitrate of silver, and the solution is filtered while hot, and left to crystallise, after addition of nitric acid. — Pale-yellow needles (Fleitmann), perfectly stable at 100°. It is almost completely precipitated from its aqueous solution by dilute nitric acid (Perrins).

| | *Dried over oil of vitriol, or at* 100°. | | Fleitmann. | | Henry. *mean.* | | Perrins. *mean.* |
|---|---|---|---|---|---|---|---|
| 40 C | 240 | ... | 60·30 | .... | 60·15 | .... 59·27 | .... 60·16 |
| 2 N | 28 | .... | 7·03 | | | | |
| 18 H | 18 | .... | 4·52 | .... | 4·75 | .... 4·84 | .... 4·57 |
| 14 O | 112 | .... | 28·15 | | | | |

C⁴⁰NH¹⁷O³,HO,NO⁵ .... 398 .... 100·00

*Chromate of Berberine.* — *Bi-acid.* — Bichromate of potash throws down from hydrochlorate of berberine a pale-yellow precipitate, difficultly soluble in water, but easily soluble in sulphuric and hydrochloric acids (Fleitmann). On adding bichromate of potash to a boiling very dilute solution of hydrochlorate of berberine, the salt crystallises almost entirely on cooling, and may be recrystallised from a large quantity of hot water. — Dissolves very slightly in cold water and in aqueous chromate of potash (Perrins).

| | *at* 100°. | | | | Fleitmann. *mean.* | | Perrins. *mean.* |
|---|---|---|---|---|---|---|---|
| 40 C | 240 | ........ | 53·86 | ........ | 54·58 | ........ | 53·71 |
| N | 14 | ........ | 3·14 | | | | |
| 18 H | 18 | ........ | 4·04 | ........ | 4·30 | ........ | 4·04 |
| 12 O | 96 | ........ | 21·55 | | | | |
| Cr²O³ | 77·6 | ........ | 17·41 | ........ | 17·24 | ........ | 17·43 |

C⁴⁰NH¹⁷O³,HO,2CrO³ .... 445·6 ....... 100·00

*Phosphomolybdic acid* throws down dirty yellow flocks from solutions of salts of berberine.

*Chloromercurate of Berberine.* — A solution of berberine in a large quantity of strong alcohol mixed with hydrochloric acid, and added boiling hot to an alcoholic solution of mercuric chloride also containing hydrochloric acid, yields, on cooling, fine yellow needles, having a silky lustre. The needles are washed with alcohol, and with a mixture of water and alcohol in succession. Thus prepared, they contain 1 at. chloride of mercury to 1 at. hydrochlorate of berberine. Their solution in a very large quantity of hot water, however, yields longer and larger crystals of a compound with 2 at. chloride of mercury (Hinterberger, *Wien. Acad. Ber.* 7, 432; *Ann. Pharm.* 82, 314).

| | *With* 1 *at.* HgCl. | | | | Hinterberger. *mean, at* 100°. |
|---|---|---|---|---|---|
| 40 C | 240 | ........ | 47·33 | ........ | 47·10 |
| N | 14 | ........ | 2·76 | | |
| 18 H | 18 | ........ | 3·55 | ........ | 3·59 |
| 8 O | 64 | ... .... | 12·62 | | |
| 2 Cl | 71 | ........ | 14·00 | | |
| Hg | 100 | ........ | 19·74 | ..-.... | 19·93 |

C⁴⁰NH¹⁷O³,HCl,HgCl .... 507 ........ 100·00

| | *With* 2 *at.* HgCl. | | | | Hinterberger. |
|---|---|---|---|---|---|
| 40 C | ................................ | 240 | ........ | 37·35 | ........ 37·70 |
| N | ................................ | 14 | ........ | 2·18 | |
| 18 H | ................................ | 18 | ........ | 2·80 | ........ 2·87 |
| 8 O | ................................ | 64 | ........ | 9·96 | |
| 3 Cl | ................................ | 106·5 | ........ | 16·58 | |
| 2 Hg | ................................ | 200 | ........ | 31·13 | ........ 30·42 |

C⁴⁰NH¹⁷O⁸,HCl,2HgCl .... 642·5 ........ 100·00

$C^{40}NH^{17}O^8,HCl,2HgCl$ .... 642·5 ........ 100·00

*Berberine and Oxide of Silver?* Nitrate of silver throws down from a hot aqueous solution of berberine (hydrochlorate?) a yellow precipitate, which may be obtained in delicate crystals from a solution in warm water (Buchner).

| | *at* 100°. | | | | Buchner. *mean.* |
|---|---|---|---|---|---|
| $C^{40}NH^{17}O^8$ | ................ | 335 | ........ | 74·28 | ........ 74·02 |
| AgO | ................ | 116 | ........ | 25·72 | ........ 25·98 |

?$C^{40}NH^{17}O^8$,AgO .... 451 ........ 100·00     100·00

Since Buchner's berberine contained hydrochloric acid, the value of the analysis is questionable.

*Hyposulphite of Berberine and Silver.* — A solution of nitrate of silver in aqueous hyposulphite of soda precipitates from cold neutral salts of berberine a yellow amorphous powder. By mixing the nitrate of silver solution with hot alcoholic nitrate of berberine, small lemon-yellow prisms are obtained on cooling. — Insoluble in water, but easily soluble in alcohol and in aqueous hyposulphite of soda, the latter solution being decomposed by boiling, with separation of sulphide of silver. The dry salt is stable at 100° (Perrins).

| | | | | | Perrins. *mean.* |
|---|---|---|---|---|---|
| 40 C | ................ | 240 | ........ | 43·16 | ........ 43·07 |
| N | ................ | 14 | ........ | 2·52 | |
| 18 H | ................ | 18 | ........ | 3·23 | ........ 3·23 |
| 14 O | ................ | 112 | ........ | 20·16 | |
| 4 S | ................ | 64 | ........ | 11·51 | ........ 11·47 |
| Ag | ................ | 108 | ........ | 19·42 | ........ 19·45 |

$C^{40}NH^{17}O^8,HO,S^2O^2 + AgO,S^2O^2$ 556 ........ 100.00

*Chloro-aurate of Berberine.* — Previously noticed by Chevallier and Pelletan. Terchloride of gold throws down from hydrochlorate of berberine an amorphous brown precipitate, which, when washed with water and dissolved in boiling dilute alcohol, crystallises in chestnut-brown needles (Perrins).

| | *at* 100°. | | | | Henry. Amorphous. | | Perrins. Crystals. (*mean.*) |
|---|---|---|---|---|---|---|---|
| 40 C | ................ | 240 | ........ | 35·57 | ........ 35·50 | ........ | 35·50 |
| N | ................ | 14 | ........ | 2·08 | | | |
| 18 H | ................ | 18 | ........ | 2·67 | ........ 2·94 | ........ | 2·74 |
| 8 O | ................ | 64 | ........ | 9·49 | | | |
| 4 Cl | ................ | 142 | ........ | 21·05 | | | |
| Au | ................ | 196·6 | ........ | 29·14 | ........ 27·75 | ........ | 29·16 |

$C^{40}NH^{17}O^8,HCl,AuCl^3$ .... 674·6 ........ 100·00

*Chloroplatinate of Berberine.* — A hot aqueous solution of hydro-chlorate of berberine is precipitated by chloride of platinum, and the precipitate is washed with cold water till the washings cease to indicate the presence of platinum on addition of iodide of potassium. — Small crystalline needles (Perrins).

| | | at 100°. | | | Fleitmann. mean. | | Kemp. |
|---|---|---|---|---|---|---|---|
| 40 C | ................................ | 240 | ........ | 44·35 | ........ | 44·39 | ........ 46·23 |
| N | ................................ | 14 | ........ | 2·59 | | | |
| 18 H | ................................ | 18 | ........ | 3·33 | ........ | 3·50 | ........ 3·68 |
| 8 O | ................................ | 64 | ........ | 11·83 | | | |
| 3 Cl | ................................ | 106·5 | ........ | 19·68 | | | |
| Pt | ................................ | 98·6 | ........ | 18·22 | ........ | 18·11 | ........ 18·05 |

C⁴⁰NH¹⁷O⁸,HCl,PtCl² .... 541·1 ........ 100·00

| | Bödeker. | | Stenhouse. | | Henry. | | Perrins. mean. |
|---|---|---|---|---|---|---|---|
| C | 45·22 | ........ | 44·87 | ........ | 44·38 | ........ | 44·33 |
| N | | ... .... | | ........ | | ........ | 2·80 |
| H | 3·92 | ........ | 3·81 | ........ | 3·57 | ........ | 3·41 |
| O | | | | | | | |
| Cl | | | | | | | |
| Pt | 17·58 | ........ | 17·54 | ........ | 17·82 | ........ | 18·21 |

In the salt prepared with berberine from barberry flowers, Ferrein found 17·87 p. c. of platinum.

*Hydrocyanate of Berberine.* — Aqueous hydrochlorate of berberine assumes a dark-red colour when mixed with cyanide of potassium, and throws down dirty-yellow flocks which, after washing with water, crystallise from alcohol in brown-yellow rhombic laminæ. Stable at 100° when dry, but not in the moist state. It dissolves slightly in water from which it does not crystallise, and is soluble in cold, and more freely in hot, alcohol. The solutions smell of hydrocyanic acid (Henry).

| | | at 100—110°. | | | Henry. |
|---|---|---|---|---|---|
| 42 C | ........................ | 252 | ........ | 69·62 | ........ 66·93 |
| 2 N | ........................ | 28 | ........ | 7·73 | |
| 18 H | ........................ | 18 | ........ | 4·97 | ........ 5·22 |
| 8 O | ........................ | 64 | ........ | 17·68 | |

C⁴⁰NH¹⁷O⁸,HCy .... 362 ........ 100·00

Contains 6·22 p. c. of cyanogen; (Henry) (calc. 7·18 p. c.).
*Hydrocyanate of Berberine with Nitric acid ?* Very dilute nitric acid colours hydrocyanate of berberine red, without liberating hydrocyanic acid. The concen-trated acid produces a red to black substance, a solution of which in water or alcohol yields red needles of (according to Henry) hydrocyanate of nitroberberine. The needles contain, at 100—110°, 60·35 p. c. C., and 4·80 H. (Henry).

*Hydroferrocyanate of Berberine.* — Precipitated by ferrocyanide of potassium from aqueous hydrochlorate of berberine. — Greenish-yellow, microscopic needles, which in the moist state decompose at 100°, evolving an odour of hydrocyanic acid. — Dissolves in 1250 parts of cold water, and slightly in hot water and alcohol (Henry).

| | at 100—120° | | | Henry. |
|---|---|---|---|---|
| $2\ C^{40}NH^{17}O^8,H^2Cy^3$............ | 750 | ........ | 96·41 | |
| Fe............ | 28 | ........ | 3·59 | ........ 3·86 |
| $2\ C^{40}NH^{17}O^8,H^2FeCy^3$ .... | 778 | ........ | 100·00 | |

*Hydroferricyanate of Berberine.* — Resembles the preceding salt, but is yellower, and after drying apple-green (Henry).

| | at 100—110° | | | Henry. |
|---|---|---|---|---|
| $3\ C^{40}NH^{17}O^8,H^3Cy^6$ ........ | 1164 | ........ | 95·41 | |
| 2 Fe ........ | 56 | ........ | 4·59 | ........ 4·30 |
| $3\ C^{40}NH^{17}O^8,H^3Fe^2Cy^6$.... | 1220 | ........ | 100·00 | |

*Hydrochlorate of Berberine with Cyanide of Mercury.* — Solutions of hydrochlorate of berberine and cyanide of mercury, mixed together while hot, deposit on cooling, yellow needles soluble in hot water and alcohol (Kohl & Swoboda, *Wien. Acad. Ber.* 9, 252; *Ann. Pharm.* 83, 340).

| | at 100° | | | Kohl & Swoboda. |
|---|---|---|---|---|
| $C^{40}NH^{17}O^8,HCl,Cy$ ........ | 397·5 | ........ | 79·90 | |
| Hg ........ | 100 | ........ | 20·10 | ........ 19·17 |
| $C^{40}NH^{17}O^8,HCl + HgCy$.... | 497·5 | ........ | 100·00 | |

*Hydrosulphocyanate of Berberine.* — Sulphocyanide of potassium throws down from concentrated hot solutions of hydrochlorate of berberine, a greenish-yellow powder, which crystallises from boiling water in siskin-yellow, and from boiling alcohol in brown-yellow needles. Dissolves in 4,500 parts of water, and in 470 parts of alcohol (Henry).

| | | | | Henry. |
|---|---|---|---|---|
| 42 C | 252 | ........ | 63·95 | ........ 61·85 |
| 2 N | 28 | ........ | 7·12 | |
| 18 H | 18 | ........ | 4·57 | ........ 4·64 |
| 8 O | 64 | ........ | 16·24 | |
| 2 S | 32 | ........ | 8·12 | ........ 8·10 |
| $C^{40}NH^{17}O^8,C^2NHS^2$ .... | 394 | ........ | 100·00 | |

Contains 14·16 p. c. of sulphocyanogen (Henry).

*Acetate of Berberine* forms golden-yellow crystals (Kemp).

*Oxalate of Berberine.* — Formed from oxalic acid and berberine. — Brownish warts formed of clusters of needles (Henry).

| | at 100—110° | | | Henry. |
|---|---|---|---|---|
| 44 C | 264 | ........ | 62·11 | ........ 60·78 |
| N | 14 | ........ | 3·29 | |
| 19 H | 19 | ........ | 4·47 | ........ 4·67 |
| 16 O | 128 | ........ | 30·13 | |
| $C^{40}NH^{17}O^8,C^4H^2O^8$ .... | 425 | ........ | 100·00 | |

*Glycocoll with Hydrochlorate of Berberine.* — A warm alcoholic solution of hydrochlorate of berberine mixed with excess of alcoholic glycocoll solidifies on cooling, from the formation of delicate pomegranate-yellow needles, which are insoluble in water (Horsford, *Ann. Pharm.* 60, 32).

|  |  |  |  |  | Horsford. |
|---|---|---|---|---|---|
| 44 C | 264 | ........ | 60·34 | ........ | 60·80 |
| 2 N | 28 | ........ | 6·40 |  |  |
| 22 H | 22 | ........ | 5·03 | ........ | 5·87 |
| 11 O | 88 | ........ | 20·12 |  |  |
| Cl | 35·5 | ........ | 8·11 |  |  |

$C^{4}H^{4}O^{3},C^{40}NH^{17}O^{8},HCl$ ....    437·5    ........    100·00

Gerhardt (it seems to me justly) doubted the correctness of this formula (Kr.).

*Succinate of Berberine.* — A solution of berberine supersaturated with succinic acid deposits brownish needles, triturable to a yellow powder. Dissolves in water and alcohol, more especially when hot (Henry).

| | at 100—110°. | | | | Henry. |
|---|---|---|---|---|---|
| 48 C | 288 | ........ | 63·57 | ........ | 61·99 |
| N | 14 | ........ | 3·09 |  |  |
| 23 H | 23 | ........ | 5·09 | ........ | 5·80 |
| 16 O | 128 | ........ | 28·25 |  |  |

$C^{40}NH^{17}O^{8},C^{8}H^{6}O^{8}$ ........    453    ........    100·00

*Tartrate of Berberine.* — Long siskin-yellow, silky needles, obtained by supersaturating berberine with the acid. — Dissolves in 130 parts of cold water or alcohol, and much more freely in the hot liquids. — Loses 1·62 p. c. of water at 100° (1 at. = 1·82 p. c. HO) (Henry).

| | Dried. | | | | Henry. |
|---|---|---|---|---|---|
| 48 C | 288 | ........ | 59·38 | ........ | 58·15 |
| N | 14 | ........ | 2·88 | ........ | 3·16 |
| 23 H | 23 | ........ | 4·75 | ........ | 5·08 |
| 20 O | 160 | ........ | 32·99 | ........ | 33·61 |

$C^{40}NH^{17}O^{8},C^{8}H^{6}O^{12}$ ....    485    ........    100·00    ........    100·00

*Tartrate of Berberine and Antimony.* — Formed, with separation of oxide of antimony, by boiling berberine with a cold saturated solution of tartar-emetic. Crystallises from the filtrate (which contains also tartrate of potash) in fibrous masses resembling wavellite, and is purified by washing with cold water or by recrystallising from alcohol (Stenhouse, *Ann. Pharm.* 129, 26).

| | In vacuo. | | | Stenhouse. | |
|---|---|---|---|---|---|
| 48 C | 288 | ........ | 46·43 | ........ | 46·46 |
| N | 14 | ........ | 2·25 |  |  |
| 22 H | 22 | ........ | 3·54 | ........ | 3·76 |
| 22 O | 176 | ........ | 28·39 |  |  |
| Sb | 120·3 | ........ | 19·39 | ........ | 19·85 |

$C^{40}NH^{17}O^{8},HO,SbO^{3},C^{8}H^{4}O^{10}$ ....    620·3    ........    100·00

*Picrate of Berberine.* — Formed from picric acid and berberine. Golden-yellow laminæ (Henry); yellowish-brown or pinchbeck-coloured shining prisms (Kemp). — Nearly insoluble in cold, and slightly soluble in boiling alcohol (Henry).

| | at 100°. | | | | Henry. |
|---|---|---|---|---|---|
| 52 C | 312 | ........ | 55·32 | ........ | 54·83 |
| 4 N | 56 | ........ | 9·93 |  |  |
| 20 H | 20 | ........ | 3·55 | ........ | 3·93 |
| 22 O | 176 | ........ | 31·20 |  |  |

$C^{40}NH^{17}O^{8},C^{12}X^{3}H^{3}O^{2}$ ....    564    ........    100·00

Berberine dissolves in *alcohol*. It is precipitated from its solutions by *charcoal*, and again extracted therefrom by alcohol (Chevallier & Pelletan).

<center>*Appendix to Berberine.*</center>

## Oxyacanthine.

POLEX. *N. Br. Arch.* 6, 271.
WITTSTEIN. *Repert.* 86, 258.
HERBERGER. *Jahrb. pr. Pharm.* 4, 82.
WACKER. *Pharm. Viertelj.* 10, 177.

Discovered by Polex in 1836. — Occurs, together with berberine, in the bark of the root of *Berberis vulgaris* (Polex), and also, together with a little berberine, in the bark of an undetermined species of *Berberis* from Mexico (Wittstein).

*Preparation.* The mother-liquor from which the berberine has been crystallised as completely as possible, in the preparation of berberine from the bark of barberry root, is diluted with 4 or 5 parts of water and precipitated with carbonate of soda; the precipitate is collected, washed with cold water, and dissolved in dilute sulphuric acid; the solution is decolorised with animal charcoal and again precipitated with carbonate of soda; and the washed precipitate is dried and dissolved in cold alcohol. From the solution thus obtained, the oxyacanthine may be recovered by evaporation, or by precipitation with water (Polex). Wittstein (and Wacker) exhausts the precipitate produced by carbonate of soda with dilute hydrochloric acid; precipitates the filtrate by ammonia; and exhausts the washed precipitate, after drying and pulverisation, with ether in a percolator. The oxyacanthine left on evaporating the ethereal solution is again dissolved in hydrochloric acid, thrown down by ammonia, and purified by crystallising its hydrochlorate, which is then decomposed by ammonia. — The portion insoluble in ether still contains a large quantity of oxyacanthine, which it gives up to ether only after first removing the humic acid present by means of water containing soda. — Oxyacanthine is difficult to obtain in the pure state, inasmuch as it oxidises in the air, especially when precipitated by ammonia (Polex). Wittstein obtained from 350 pounds of the fresh bark 13 drachms of oxyacanthine.

*Properties.* Dazzling white powder, turning yellow in sunlight; under a magnifying-power of 130 diameters it is seen to consist of amorphous round granules (Wacker). According to Buchner, jun., it is converted, by digestion with a little ether or alcohol, into fine needles and prisms. It is deposited from an alcoholic solution in resinous laminæ, or if the solution is mixed with a quantity of water barely sufficient to produce turbidity and evaporated, in the form of a yellowish crystalline crust (Polex). Has a pure bitter taste and an alkaline reaction. — Loses 3·13 p. c. of its weight at 100°, and not more at 120°. Melts to a yellow liquid at 139° (Wacker).

|  |  |  | *Calculation according to Wacker.* |  |  | Wacker. at 100°. |
|---|---|---|---|---|---|---|
| 32 C | ..................... | 192 | ........ | 60·56 | ........ | 60·26 |
|  | N..................... | 14 | ........ | 4·42 | ........ | 4·51 |
| 23 H | ................... | 23 | ........ | 7·26 | ........ | 7·53 |
| 11 O | ..................... | 88 | ........ | 27·76 | ........ | 27·70 |
| C³²NH²³O¹¹ | ........ | 317 | ........ | 100·00 | ........ | 100·00 |

This formula is, doubtless, incorrect; but the analysis does not admit of the calculation of any other probable one.

*Decompositions.* 1. When submitted to *dry distillation* it yields aqueous vapour, a brown thick empyreumatic oil and ammonia, and evolves an odour of animal oil, whilst a very porous charcoal remains behind (Polex). — 2. Melts to an oil in the *fire* and burns rapidly with a luminous flame. — 3. Dissolves in *oil of vitriol*, forming a brown-red solution which, on warming, assumes a splendid red colour, afterwards turning brown. — 4. Softens to a resin in strong *nitric acid* and dissolves with yellow colour, which changes to a fine purple-red on warming. The solution turns yellow on boiling, with liberation of nitric oxide and formation of oxalic acid, and when diluted with water deposits yellow flocks, which behave like berberine (Polex). — 5. Dissolves in *chlorine-water*, forming a yellow solution, which is rendered darker, but not turbid, by ammonia. — 6. Reduces sesquioxide of chromium from *bichromate of potash* and sulphuric acid. — 7. *Iodic acid* in contact with oxyacanthine is coloured yellow and deposits iodine (Wacker).

Oxyacanthine is nearly insoluble in *water*.

It combines with *acids* to form easily crystallisable salts soluble in water and alcohol (Polex). From solutions of the salts, ammonia, carbonate of ammonia, caustic alkalis and their carbonates, and lime-water, throw down oxyacanthine as a white precipitate, soluble in a large excess of ammonia and more easily soluble in excess of caustic potash (Wacker). The hydrochlorate is precipitated white by iodide of potassium, chloride of mercury, sulphocyanide of potassium, and ferrocyanide of potassium; yellowish-white by phosphomolybdic acid and tannic acid; yellow-orange by nitrate of palladium; clay-coloured by chloride of gold, and sulphur-yellow by ferricyanide of potassium (Wacker). The acetate is precipitated also by nitrate of silver, tartar-emetic, and chloride of tin (Polex).

*Sulphate of Oxyacanthine.* — Neutral white nodules (Wacker), or tufts of needles (Polex), easily soluble in water and alcohol.

|  |  | at 100°. |  |  |  | Wacker. |
|---|---|---|---|---|---|---|
| C³²NH²³O¹¹,HO | ............ | 326 | ........ | 89·07 |  |  |
| SO³ | ............ | 40 | ........ | 10·93 | ........ | 11·2 |
| C³²NH²³O¹¹,HO,SO³ | .... | 366 | ........ | 100·00 |  |  |

*Hydrochlorate of Oxyacanthine.* — Clusters of needles (Polex), or neutral white nodules, easily soluble in nodules and alcohol (Wacker).

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| $C^{32}NH^{23}O^{11}$ | ............ | 317·0 | ........ | 89·78 | |
| HCl | ............ | 36·5 | ........ | 10·32 | ........ 9·33 |
| $C^{32}NH^{23}O^{11}$,HCl | .... | 353·5 | ........ | 100·00 | |

Wacker supposes it to contain 4 at. of water.

*Iodomercurate of potassium* throws down from oxyacanthine a yellowish-white precipitate, which remains amorphous (Delffs).

*Nitrate of Oxyacanthine.* — Warts and needles, more difficultly soluble in water than the sulphate and hydrochlorate (Wacker).

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| $C^{32}NH^{23}O^{11}$ | .............. | 317 | ........ | 83·42 | ........ 77·88 |
| $HO,NO^5$ | .............. | 63 | ........ | 16·58 | |
| $C^{32}NH^{23}O^{11}$,$HO,NO^5$ | .... | 380 | ........ | 100·00 | |

Wacker supposes this salt also to contain 4 at. of water.

*Chloroplatinate of Oxyacanthine.* — Pale grey-yellow precipitate.

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| $C^{32}NH^{23}O^{11}$,$HCl^3$ | ............ | 424·5 | ........ | 81·13 | |
| Pt | ............ | 98·7 | ........ | 18·87 | ........ 18·81 |
| $C^{32}NH^{23}O^{11}$,$HCl,PtCl^2$ | .... | 523·2 | ........ | 100·00 | |

*Acetate of oxyacanthine* is not crystallisable.

*Oxalate of Oxyacanthine.* — Needles, difficultly soluble in water. Contains, at 100°, 10·30 p. c. of anhydrous oxalic acid (Wacker).

*Picrate of Oxyacanthine.* — Previously observed by Kemp (*Repert,* 71, 164). — Lemon-yellow precipitate, soluble in a large quantity of water, and in dilute acids and alcohol (Wacker).

Oxyacanthine dissolves easily in weak and in absolute *alcohol* (Polex); in 30 parts of cold, and 1 part of boiling alcohol (Wacker). — Dissolves in 4 parts of boiling, and 125 parts of cold *ether*, in all proportions in *chloroform*, and in *volatile and fixed oils* (Wacker).

*Primary Nucleus* $C^{40}H^{28}$; *Oxy-azo-nucleus* $C^{40}N^2H^{22}O^2$.

# Cinchonine.

$$C^{40}N^2H^{24}O^2 = C^{40}N^2H^{22}O^2,H^2.$$
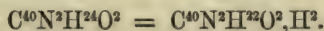
For the literature relating to Cinchonine and Quinine in common, see QUININE.

REGNAULT. *Ann. Pharm.* 26, 15; *J. pr. Chem.* 16, 262.
LIEBIG. *Ann. Pharm.* 26, 50.
LAURENT. *N. Ann. Chim. Phys.* 19, 365; *Ann. Pharm.* 62, 99; *J. pr. Chem.* 40, 404; *Kopp's Jahresber.* 1847 and 1848, 615 and 617 — *Compt. rend.* 20, 1116; *N. Ann. Chim. Phys.* 24, 303; *Ann. Pharm.* 69, 8; *J. pr. Chem.* 46, 52 — *Compt. rend.* 23, 811.

HLASIWETZ.   *Wien. Acad, Ber.* 1850, 1, 9, and 276; *Ann. Pharm.* 77,
    49; *J. pr. Chem.* 51, 409; *Pharm. Centr.* 1851, 74; *Kopp's Jahresber.*
    1850, 420.
A. ERDMANN.   *Ann. Pharm.* 100, 341; abstr. *J. pr. Chem.* 70, 422;
    *Kopp's Jahresber.* 1856, 545.
H. HAHN.   *N. Br. Arch.* 96, 33; *Kopp's Jahresber.* 1858, 372.
SCHWABE (& LÖSCHE).   *N. Br. Arch.* 103, 273; abstr. *N. J. Pharm.*
    38, 389; *Chem. Centr.* 1860, 936; *Kopp's Jahresber.* 1860, 362.
O. HESSE.   *Ann. Pharm.* 122, 226.

Discovered by Pelletier & Caventou in 1820. — Occurs in the true
cinchona barks; most abundantly in the grey and brown barks; to a
less extent, together with more quinine, in the red and yellow barks,
and in small quantity in calisaya bark. For more exact details see
*Quinine.*

A. Erdmann described as *Huanokine* a base prepared from *China Huanoco plana*,
which he distinguished from cinchonine chiefly on the ground of its susceptibility of
sublimation: he seems, however, to have compared it with commercial cinchonine
containing quinidine or cinchonidine, and not with the pure alkaloïd. Seeing that
this body possesses, according to Gössmann, the same composition, and according to
De Vrij (*N. J. Pharm.* 32, 328), the same molecular rotatory power as cinchonine,
and since, moreover, its hydriodate resembles the hydriodate of cinchonine, and
its combinations exhibit, so far as can be ascertained from Hahn's approximate
and not strictly accurate measurements, the same crystalline form as salts of cincho-
nine, there is no reason to suppose that it differs from this last-named base. —
Schwabe's *Betacinchonine*, which was discovered in working with crude commercial
quinoïdine, is also, according to Hesse, to be identified with cinchonine. Lösche's
measurements of the crystals are not sufficiently exact to establish any difference in
form; and Schwabe's statements either agree with those of other authors on cincho-
nidine, or may be explained by the supposition that he did not, in all cases, work with
a pure substance (free from quinidine). Betacinchonine is coloured yellow by chlorine-
water and ammonia; but ferrocyanide of potassium alone, or together with chlorine-
water, turns the sulphate red, whereupon ammonia produces a green coloration.
In excess of acid, it forms only mono-acid salts, the solutions of which, when shaken
in not too concentrated a state, with ammonia and ether, form two clear layers, the
upper containing the betacinchonine. [This statement does not accord with the fact
of the difficult solubility of betacinchonine in ether (Kr.)] For Schwabe's other
statements see *Cinchonine.* — Schützenberger affirms the existence of a cinchonine of
the formula $C^{36}N^2H^{22}O^4$ (*Compt. rend.* 46, 895).
    The base observed by Gruner (*Br. Arch.* 12, 156) in *China flava* [*China de
Carthagena dura* (Wiggers)] is not sufficiently characterised to distinguish it from
cinchonine. It forms delicate, tasteless needles, easily soluble in alcohol but insoluble
in ether. The sulphate forms slightly bitter 4-sided prisms, which are easily soluble
in water, and contain 12·81 p. c. of sulphuric acid.

Cinchonine is obtained as a secondary product in the preparation of
quinine. When it is required to be prepared specially, huanoco-bark
is employed, and the following, or a similar, process is adopted :—
    Four pounds of the coarsely powdered bark are boiled for some
hours with 54 pounds of water, to which 2 ounces of hydrochloric acid
of sp. gr. 1·2 have been added. The decoction is pressed, and the
residue again boiled twice, the last time with only half the quantity of
acidulated water; and the united liquids are evaporated down to 12
pounds, filtered, and mixed with sufficient caustic soda to produce an
alkaline reaction. The precipitate thereby produced is washed, dis-
solved in hydrochloric, or better, in acetic acid, and again precipitated,
by which means the colouring matter is got rid of. The precipitate is
then dried and exhausted by boiling with alcohol, from which the cin-

chonine crystallises on concentration. It is still to be purified by recrystallisation, with aid of animal charcoal (A. Erdmann).

*Purification.* Commercial cinchonine is mostly contaminated with cinchonidine or quinidine (De Vrij). To purify it, the larger yellowish crystals obtained in the manufacture of quinine are powdered, washed with a large quantity of cold alcohol, and converted into sulphate, which is then purified by recrystallisation and decomposed by ammonia. The pure alkaloïd is, lastly, crystallised from alcohol (Hesse).

*Properties.* White, transparent needles, permanent in the air, and containing no water of crystallisation (Pelletier & Caventou). Oblique prismatic (monoclinic). $u, t, i$ (fig. 106). The crystals are elongated in the direction of the clinodiagonal axis. $u : u = 109°\ 5·5'$; $t : i$ in front $= 107°\ 19'$; $t : i$ behind $= 72°\ 41''$; $i : u = 100°\ 5·5'$; $l$ sharply curved, $m$ plane; cleavable parallel to $l$, less perfectly parallel to $m$ (Schabus). $u : u = 110°\ 22'$; $u : t = 124°\ 35'$; $t : i = 108°\ 30'$ (Delffs, *Jahrb. pr. Pharm.* 8, 377). $u : u = 109°$; $u : t = 125°$; $t : i = 110°$; $i : u = 90°$ (!) (Hahn). According to Lösche, monoclinic. $p, m, i$ (fig. 53). $i : i$ above $= 119°$; $i : p = 120·5°$. — Cinchonine melts only as it begins to decompose, and volatilises partly undecomposed, especially when moist (Pelletier & Caventou, *J. Pharm.* 7, 305; Robiquet). Precipitated or crystallised cinchonine undergoes no alteration at 165°; it partly sublimes at 220°, and the rest melts at 240—250° to a brown mass, which solidifies on cooling (Hesse). Schwabe's cinchonine melted, at 150°, to an oil which cooled to a crystalline solid : that of Duflos melted at 161°, without loss of weight, and on further heating sublimed partially in dazzling white needles, in the same manner as benzoic acid (Duflos). In the air the vapour forms light white flocks (Fr. Esenbeck, *Ann. Pharm.* 6, 319; Erdmann); in hydrogen or ammonia-gas, shining prisms an inch long are obtained (Hlasiwetz). Cinchonine turns reddened litmus blue; tastes slightly bitter after some time (Pelletier & Caventou). Rotates a ray of polarised light to the right; $(\alpha)\ r = 237·5°$ in alcoholic solution, and to a less extent when dissolved in acids. Ammonia seems to restore the original rotatory power (Bouchardat, *N. Chim. Phys.* 9, 213). Rotatory power of Pelletier's cinchonine dissolved in hydriodic acid; $(\alpha)\ j = 242·58°$; of Erdmann's huanokine $= 242·55°$ (De Vrij); of both, dissolved in hydrochloric acid $= 237·3°$ (Hahn).

| | | | | Pelletier.<br>& Dumas. | | Liebig.<br>*mean.* | | Regnault.<br>*mean.* |
|---|---|---|---|---|---|---|---|---|
| 40 C | 240 | ........ | 77·92 | ........ | 76·97 | ........ | 76·36 | ........ | 76·59 |
| 2 N | 28 | ........ | 9·09 | ........ | 9·02 | ........ | 8·87 | ........ | 9·48 |
| 24 H | 24 | ........ | 7·79 | ........ | 6·22 | ........ | 7·38 | ........ | 7·72 |
| 2 O | 16 | ........ | 5·20 | ........ | 7·79 | ........ | 7·39 | ........ | 6·21 |
| $C^{40}N^2H^{24}O^2$ | 308 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

| | Gerhardt.<br>(*Rev. scient.* 10, 192.) *mean.* | | Laurent.<br>*mean.* | | Hlasiwetz.<br>*mean* (10). | | Gössmann.<br>*mean.* | | Schwabe.<br>*mean.* |
|---|---|---|---|---|---|---|---|---|---|
| C | 77·63 | ........ | 77·29 | ........ | 78·02 | ........ | 77·61 | ........ | 77·29 |
| N | | ........ | | ........ | | ........ | 8·83 | ........ | 9·09 |
| H | 7·99 | ........ | 7·49 | ........ | 7·66 | ........ | 7·73 | ........ | 7·87 |
| O | | ........ | | ........ | | ........ | 5·83 | ........ | 5·75 |
| | | | | | | | 100·00 | ........ | 100·00 |

Gössmann analysed crystals of huanokine ; Schwabe crystallised betacinchonine. — The formula, according to Dumas, is $C^{40}N^2H^{20}O^3$ ; according to Laurent $C^{38}N^2H^{22}O^2$ ; according to Liebig $C^{20}NH^{11}O$. The above formula was shown by Regnault to be the correct one. It cannot be halved either for this body or for the two other alkaloïds of cinchona, as in that case, the mono-acid salts, formed to some extent in an excess of acid, would have to be regarded as a basic. Moreover, the behaviour of the base with bromine, and with iodide of ethyl, chloride of acetyl, and sulphuric acid, makes the halving of the formula impossible. See Laurent and Gerhardt (*Compt. chim.* 1849, 167).

*Decompositions.* 1. Melted cinchonine turns brown on continued *heating* (Duflos), takes fire at a higher temperature, and leaves a light, easily combustible charcoal (Merck). Besides the sublimate of cinchonine (see above) a carmine-red product is obtained (Wigaud, *N. Br. Arch.* 115, 230).

When cinchona-bark is heated, at first gently and afterwards gradually to redness, in a test-tube held in a horizontal position, white vapours and water are given off, followed by a reddish vapour, which is at first deposited in the form of a powder, then condenses in fine carmine-red oily drops and streaks, and at last a brown tar is obtained. The carmine-red oil turns brown-red in the air, and has a bitter, burning taste ; it is thrown down from its alcoholic solution by water in the form of a resin, and contains acetic acid, volatile bases, a neutral oil, and empyreumatic resin. This behaviour is exhibited only by the true cinchona-barks, not by false cinchona-barks or by those from which the cinchona-bases have been extracted by acids. The red body is not formed by heating the cinchona-bases *per se*, but is readily obtained when they are heated with organic acids (Grahe, *Chem. Centr.* 1858, 97). Batka (*Chem. Centr.* 1859, 865) obtained the red distillate from cinchona-bases only in presence of woody fibre, starch, gum, dextrin, or sugar, and not under the conditions mentioned by Grahe ; Wigand (*N. Br. Arch.* 115, 230) obtained it from pure cinchonine, and also from the sulphate, but not from pure quinine. See also *N. Br. Arch.* 121, 265.

2. Solutions of cinchonine-salts, when exposed to *sunshine*, even for a few hours, assume a dark red-brown colour, and undergo the same decomposition as when heated (Pasteur). See below.

3. Cinchonine in combination with nitric acid is rapidly decomposed by the *electric current* (obtained from 6 pairs of Bunsen elements), the liquid becoming brown, and evolving, at the positive pole, oxygen, and afterwards also carbonic acid and nitric oxide, and at the negative pole hydrogen, nitrogen, and ammonia. After 24 hours the liquid in which the positive pole is placed contains unchanged nitrate of cinchonine, while that surrounding the negative pole is of a red-brown colour, and contains formic acid, ammonia, chinoline (xiii, 243), and resin precipitable by potash, and is found to have deposited a large quantity of resin soluble in alcohol and nitric acid. — Sulphate of cinchonine is scarcely decomposed by the electric current. The hydrochlorate evolves chlorine, oxygen, and hydrogen, and yields crystals of a mixture of mono- and bi-chlorocinchonine (v. Babo, *J. pr. Chem.* 72, 73). See also Hlasiwetz & Rochleder (*Wien. Acad. Ber.* 5, 447).

4. Cinchonine, when acted upon by *nitrous acid*, is capable of taking up 2 at. of oxygen, and forming a body isomeric with quinine (Schützenberger, *Compt. rend.* 46, 895 ; *J. pr. Chem.* 74, 76). Cinchonine is not coloured by strong nitric acid (Merck ; Duflos). *Mercurous nitrate* colours cinchonine (and quinine) yellow (Lassaigne & Labaillif). — 5. Cinchonine is less easily attacked than quinine (which see) by permanganate of potash (Cloëz & Guignet).

6. By treating cinchonine with a mixture of *peroxide of lead, sul-*

*phuric acid*, and water, a dark-violet mass, E. Marchand's *cinchonetin*, is obtained (*N. J. Pharm.* 4, 27).

On boiling sulphate of cinchonine with water and excess of peroxide of lead, with addition of dilute sulphuric acid, so long as a filtered test-portion of the liquid is precipitated by ammonia, the liquid assumes a dark colour, and evolves carbonic acid copiously; and if it be then saturated with litharge, the solution filtered and evaporated to dryness, and the residue again dissolved, freed from lead by hydrosulphuric acid, and evaporated, the cinchonetin remains behind. It is of a dark-violet, or in thin films, of a yellow-red colour, translucent, and bitter. Melts on heating, evolving white non-ammoniacal fumes; burns with a smoky flame, and leaves a difficultly combustible charcoal. Dissolves in oil of vitriol, forming a red solution, from which it is not precipitated by water. Deliquesces in the air, and dissolves in water, or better in alcohol, but not in ether. Basic acetate of lead precipitates the aqueous solution violet. — By the further action of peroxide of lead and sulphuric acid, it is converted into colourless products, amongst which acetic acid appears to occur (E. Marchand, *J. Chim. méd.* 20, 362).

7. Cinchonine in contact with dilute *sulphuric acid* and *zinc*, takes up 2 at. of hydrogen, and is converted into hydroquinine (Schützenberger). — 8. By dissolving it in fuming *sulphuric acid*, cinchonine-sulphuric acid is formed (Schützenberger). Oil of vitriol does not colour cinchonine, even when hot (Guy; Merck; Duflos).

9. The *salts of cinchonine* fuse, for the most part, when heated, and immediately undergo decomposition, the sulphate yielding thereupon a brilliant red resin; but on heating the same salt to 120—130° with water and sulphuric acid (or on heating a salt the melting-point of which lies below the temperature of decomposition) cinchonicine is formed (Pasteur).

After cinchonine had been heated too strongly and with too large a quantity of sulphuric acid, in preparing the sulphate, a portion only crystallised from the solution, the rest remaining as a brown mother-liquor, from which alkalis precipitated a dark-brown, intensely bitter, turpentine-like mass. By repeatedly dissolving this mass and finally precipitating it with ammonia, a black substance was removed, and the base was obtained as a nearly white tenacious precipitate, capable of further purification by charcoal. The body thus obtained is tough, resembles quinoïdine, is soluble in all proportions in alcohol, but insoluble in water and absolute ether. It neutralises acids completely, and is precipitated from its solutions by alkaline carbonates. The hydrochlorate forms with hyposulphite of soda a dark red-brown oil, but no crystals; it yields a pale brown-yellow, loose, crystalline platinum-salt, containing 23·5 to 25 p. c. of platinum (Winckler, *Repert.* 98, 381; *Jahrb. pr. Pharm.* 15, 281).

10. Cinchonine assumes a dirty-yellow colour in vapour of *iodine* (Donné). On triturating 1 part of iodine with 2 parts of cinchonine, dissolving the mixture in alcohol of 36°, and allowing the solution to evaporate spontaneously, there separate first iodocinchonine, and afterwards mushroom-shaped crystals of hydriodate of cinchonine. If the latter be removed by hot water, the iodocinchonine remains as a dark, saffron-yellow, friable, slightly bitter mass, which softens at 25° and melts at 80°. It contains 28·87 p. c. of iodine and 71·13 of cinchonine (equal numbers of atoms requiring 70·81 cinchonine and 29·19 iodine); dissolves very slightly in boiling water, but freely in alcohol and ether, and is decomposed by successive treatment with acids and alkalis. — When solutions of hydriodate and of iodate of cinchonine are mixed

together, iodocinchonine separates, more especially on concentration, or immediately on addition of an acid, in the latter case together with free iodine (Pelletier, *Ann. Chim. Phys.* 63, 181 ; *Ann. Pharm.* 22, 125). See also Thomson, (*N. J. Pharm.* 8, 275). — Tincture of iodine throws down from hydrochlorate of cinchonine a dense brown precipitate (Planta), which becomes crystalline on standing (Seligsohn). The precipitate thrown down by biniodide of potassium from sulphate of cinchonine is decomposed by hyposulphite of soda, with formation of hydriodic acid and cinchonine, and when freshly precipitated, requires for its decomposition the same quantity of hyposulphite as would be required to convert the iodine contained in it into hydriodic acid (Wägner, *Dingl.* 161, 40). — Aqueous *periodic acid* is decomposed by cinchonine, with liberation of iodine (Bödeker). — Cinchonine, *sulphuric acid,* and *iodine* yield iodocinchonine (Herapath). See below.

11. Cinchonine assumes an orange-yellow colour in *vapour of bromine* (Donné). Moist bromine forms with bi-hydrochlorate of cinchonine, mono- and sesqui-bromocinchonine ; and on warming with excess of bromine, bi-bromcinchonine is formed (Laurent). Strecker obtained only the last product. — 12. *Chlorine* passed into a warm, concentrated aqueous solution of hydrochlorate of cinchonine, throws down bichlorocinchonine (Laurent). Pure cinchonine, or sulphate of cinchonine, suspended in water, is less attacked than quinine when treated with a stream of chlorine ; the solution, which is of a less deep-red colour, and not green even with excess of chlorine, deposits flocks, an alcoholic solution of which leaves, on spontaneous evaporation, a brick-red mass (Pelletier, *J. Pharm.* 24, 163). Cinchonine dissolves in chlorine-water, without apparent change (Leers), and even on passing chlorine for ten minutes into cinchonine dissolved in 400 parts of water acidulated with sulphuric acid, the solution remains colourless and clear (Lepage). Ammonia precipitates the solution in chlorine-water, white (Leers), whereupon dilute acids colour it yellow-red, and after 12 hours a brown precipitate is formed (André, *J. Pharm.* 22, 134).

13. When cinchonine is added to fused *hydrate of potash*, and the mass is more strongly heated, it turns brown, puffs up from evolution of hydrogen, and yields a distillate of water and chinoline, the browned alkaloïd disappearing only partially, and some of the potash being converted into carbonate (Gerhardt, *N. Ann. Chim. Phys.* 7, 251). No ammonia, or only a trace, is produced in this reaction (Gerhardt). The distillate contains pyrrol (xv, 5) ; pyridine (x, 406) ; picoline (xi, 263) ; lutidine (xii, 337) ; collidine (xiii, 148); chinoline (xiii, 243) ; and lepidine (xiv, 103), the latter in larger quantity; also dispoline, $C^{22}NH^{11}$, and two unnamed bases $C^{26}NH^{15}$, and $C^{28}NH^{17}$ (Gr. Williams). Stenhouse employs this reaction for the detection of cinchonine and quinine in barks. — When hydrate of soda is used, no cyanide of sodium is formed (Rochleder, *Ann. Pharm.* 63, 201).

13. Cinchonine heated to 200° in a sealed tube with alcohol, turns black, does not evolve gas, but forms a small quantity of ether (Reynoso (*Compt. rend.* 42, 686). — 14. *Iodide of methyl* combines with cinchonine to form iodide of methyl-cinchonine (Stahlschmidt) ; *chloride of acetyl* and *chloride of benzoyl* form chloride of acetyl-cinchonine and chloride of benzoyl-cinchonine (Schützenberger). — 15. When cinchonine is heated with chloride or iodide of mercury, with tartaric,

oxalic, or phosphoric acid, with chloride of carbon, $C^2Cl^4$, or with iodide of ethyl or iodide of amyl, red or violet-red colouring matters are produced, which are soluble in alcohol, wood-spirit, and ether, and are not altered by dilute acids (Köchlin, *Rép. Chim. appliquée,* 3, 380 ; *Kopp's Jahresber,* 1861, 951). — 16. Cinchonine is decomposed in the animal organism, as, after the administration of 10 grains of the hydrochlorate, it is not found in the urine (Seligsohn).

According to Hlasiwetz, chlorine, oxide of manganese and sulphuric acid, permanganic acid, the chlorides of phosphorus, boiling acid solutions of platinum, as well as emulsin, are either without action on cinchonine, or form with it resinous bodies, from solutions of which the cinchonine is precipitated by ammonia.

*Combinations.* Cinchonine dissolves in 3810 parts of *water* at 10°, and in 3670 parts at 20° (Hesse). It dissolves in 2500 parts of boiling water, the solution becoming opalescent on cooling (Pelletier and Caventou. Riegel, *N. Br. Arch.* 70, 197), and depositing only traces of cinchonine (Hesse). The cooled solution does not exhibit any reactions, except a white turbidity with tincture of galls (Duflos).

Cinchonine combines readily with *phosphorus,* and forms with *sulphur* a grey brittle mass, which is decomposed by sulphuric acid, with evolution of hydrosulphuric acid.

Cinchonine dissolves in aqueous *ammonia* much less easily than the other cinchona-bases. The precipitate produced by ammonia in a saturated solution of the sulphate does not dissolve in excess of ammonia in the cold (Kerner, *Anal. Zeitschr.* 1, 155). — It is insoluble in aqueous *alkalis.*

*With Acids.* Cinchonine completely neutralises even the strongest acids, forming mono- and bi-acid salts, which are for the most part crystallisable. Mono-acid salts are obtained only by employing an excess of cinchonine, and filtering when the solution exhibits an alkaline reaction (De Vrij). The salts have a powerful and persistent bitter taste. Their solutions are precipitated by caustic alkalis and their carbonates and bi-carbonates, and by magnesia, ammonia, and carbonate of ammonia, the cinchonine being thrown down in the form of a dense, white, pulverulent precipitate, which does not dissolve to any great extent in excess of the precipitant (Pelletier & Caventou ; v. Planta). The precipitate becomes crumbly on standing for some time (Schwabe ; Hesse). A solution of cinchonine to which acetic acid has been added, is precipitated by bicarbonate of soda only on heating, carbonic acid being evolved (Hesse). According to Riegel (*Jahrb. pr. Pharm.* 25, 340) acetic acid does not prevent the precipitation when the salt is dissolved in 300 parts or more of water. Pentasulphide of sodium throws down from hot solutions of cinchonine, a white pulverulent mixture of sulphur and cinchonine (Palm, *Russ. Pharm. Zeitschr.* 1863, 342 ; *Böttg. Notizblatt,* 19, 112). — Solutions of cinchonine-salts containing excess of acid are not fluorescent (Raupp, *Repert,* 33, 466). In the voltaic circuit they deposit cinchonine at the negative pole (Stratingh).

*Determination of Cinchonine in its Salts.* The finely powdered salt is heated with excess of ammonia, and the liquid evaporated to 6 cub. cent. when $\frac{1}{2}$ gramme of the salt is employed. After adding a little

ammonia, the precipitate is allowed to stand for a few hours, and is then washed with an aqueous solution of cinchonine containing ammonia (Hesse).

*Carbonate of Cinchonine.* — The cinchonine thrown down by carbonate of potash from soluble salts of cinchonine retains a little carbonate of potash, but is free from carbonate of cinchonine (Langlois, *Ann. Pharm.* 32, 106). Freshly precipitated cinchonine suspended in water, dissolves less easily than quinine when treated with a stream of carbonic acid, and afterwards crystallises free from carbonic acid on standing in the air (Langlois, *N. Ann. Chim. Phys.* 41, 89).

*Phosphate of Cinchonine.* — Phosphate of soda throws down from hydrochlorate of cinchonine a dense granular precipitate, which is converted into needles on standing (v. Planta). — A solution of cinchonine in dilute phosphoric acid deposits, on spontaneous evaporation, well-formed crystals, which easily effloresce, and are more soluble in alcohol than in water (Schwabe). — Phosphoric acid and excess of cinchonine yield concentric prisms, very easily soluble in water (Hesse).

|  |  |  |  |  | Hesse. |
|---|---|---|---|---|---|
| $2C^{40}N^2H^{24}O^2$ | ........ ............... | 616 | ........ | 66·23 | ........ 66·68 |
| 24 HO | ....................... | 216 | ........ | 23·22 | ........ 22·95 |
| $PO^5,3HO$ | .......... ............... | 98 | ........ | 10·55 | |
| $2\ C^{40}N^2H^{24}O^2,3HO,PO^5 + 24$ aq. | .... | 930 | ........ | 100·00 | |

*Hyposulphite of Cinchonine.* Formed in a mixture of cinchonine, alcohol, and hydrosulphate of ammonia, on standing in the air (How). — From a moderately strong solution of hydrochlorate of cinchonine hyposulphite of soda almost immediately throws down small four-sided prisms (Winckler, *Jahrb. pr. Pharm.* 15, 286). Large, colourless, four-sided prisms (How). White rhombic prisms (Hesse), which give off 2·31 p. c. of water at 106° (1 at. = 2·41 p. c.) (How), 4·67 p. c. = 2 at., at 110° (Hesse). Neutral. Dissolves in 157 parts of water at 16° (Hesse), in 205 parts of cold, and easily in hot water (H. How, *N. Edin. Phil. J. new series* 1, 47; *Pharm. Centr.* 1858, 94).

|  | *Air-dried.* |  |  |  | Hesse. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | .......................... | 308 | ........ | 80·42 | ........ 80·69 |
| $S^2O^2,HO$ | .......................... | 57 | ........ | 14·88 | |
| 2 aq. | .......................... | 18 | ........ | 4·70 | ........ 4·67 |
| $C^{40}N^2H^{24}O^2,HO,S^2O^2 + 2$ aq. | .... | 383 | ........ | 100·00 | |

|  | *at* 100°. |  |  |  | How. |
|---|---|---|---|---|---|
| 40 C | ........................ | 240 | ........ | 65·75 | ........ 64·98 |
| 2 N | ........................ | 28 | ........ | 7·67 | |
| 25 H | ........................ | 25 | ........ | 6·85 | ........ 7·05 |
| 5 O | ........................ | 40 | ..... ... | 10·96 | |
| 2 S | ..... ................ | 32 | ........ | 8·77 | ....... 8·91 |
| $C^{40}N^2H^{24}O^2,HO,S^2O^2$.... | | 365 | ........ | 100·00 | |

*Hyposulphate of cinchonine* behaves in the same way as the quinine-salt (Heeren).

*Sulphate of Cinchonine.* — A. *Mono-acid salt.* — Obtained from sulphuric acid and excess of cinchonine in hard, transparent crystals. Prisms of the oblique prismatic (monoclinic) having a vitreous lustre

(Delffs, Schabus). *Fig. 91.* $u : u' = 96° 30'$; $u : i$ about $= 91° 23'$. Cleavable parallel to $u$ and $u'$. The $t$-faces are curved and but slightly reflective (Delffs, *Jahrb. pr. Pharm.* 8, 377). $t$, $z$, $u$, $i$, (fig. 107); $z$ predominating over $u$; $i : t$ (= $u : u'$ of Delffs) $= 96° 43' 5''$ [$= 97°$ (Baup)]; $i : t$ behind $= 83° 16' 5''$; $t : z = 112° 37'$; $i : u$ (= $u : i$ of Delffs) $= 90° 33'$; $i : z = 92° 35'$. The faces parallel to the cleavage-planes exhibit a high pearly lustre. Semi-transparent; of the hardness of rock-salt (Schabus, *Bestimm.* 74). According to Pelletier & Caventou, rectangular; according to Lösche, four-sided, most probably rectangular prisms of the right prismatic (trimetric) system, $t$, $m$ (fig. 73) terminated above by the face $y$. $y : y$ above $= 136°$; $y : m = 112°$ (Lösche); these two angles are evidently equal to $z : z$ and $t : z$ of Schabus.

The salt heated to 100° becomes electric when rubbed, and exhibits a pale-green light, fainter than that of the quinine-salt (Stratingh; Pelletier; Dumas). The crystals lose their water at 100°, melt at a little over 100° like wax, decompose at a higher temperature, with fine red coloration, and burn with an odour almost like that of burning animal matter (Pelletier & Caventou, *J. Pharm.* 7, 305, Robiquet; Stratingh). Neutral. Very bitter.

Sulphate of cinchonine easily forms supersaturated solutions with water, but it is difficult to obtain a saturated solution by agitation with cold water (Hesse). Dissolves in 54 parts of water (Baup), at 15° (Kerner), at $18\frac{3}{4}°$ (Abl). Dissolves in 65·5 parts of water at 13° (Hesse), in 75 parts at 13°, and in 14 parts of hot water (Schwabe). — Dissolves in 5·8 parts of 80 p. c. alcohol at 11° (Hesse); in 6·5 parts of alcohol of sp. gr. 0·85 at 13° (Bauss); in 13·6 parts of cold, and 1·5 parts of boiling alcohol of 80 p. c. (Schwabe). Soluble in 33·3 parts of chloroform at 17·5° (Schlimpert, *N. Br. Arch.* 100, 152). Insoluble in ether.

| | Air-dried. | | | Baup. | Regnault. | Schwabe. | Hesse.<br>*Laminæ.* | *Crystals.* |
|---|---|---|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | .... | 308 | .... | 82·14 .... | .... | .... | .... | 82·20 |
| $SO^3$ | .... | 40 | .... | 10·66 .... | 10·91 .... | .... | 10·67 .... | 10·81 .... 10·86 |
| HO | .... | 9 | .... | 2·40 | | | | |
| 2 aq. | .... | 18 | .... | 4·80 .... | 4·67 .... | 4·98 .... | 4·66 .... | 4·78 .... 4·64 |

375 .... 100·00

The dry salt contains 11·52 p. c. of sulphuric acid (calc. 11·20 p. c.) (Pelletier & Caventou), 66·20 p. c. C., and 7·33 H. (Regnault) (calc. 67·22 p. c. C., 7·00 H.)

B. *Bi-acid.* — The salt A is evaporated with dilute sulphuric acid till a pellicle forms on the surface, and the product is purified by recrystallisation. Transparent rhombic octahedrons, frequently truncated at the summits, very easily cleavable parallel to the principal axis (Baup). Diclinic? Rectangular, four-sided prisms, $a$, $b$, with an end-face $c$, resting obliquely on $u$. Angle $a : c = 83° 50'$; $b : c = 95° 50'$ (Brooke, *Ann. of Phil.* 22, 375). — Effloresces only slightly in warm dry air, but more rapidly than A when heated. Dissolves in 0·46 parts of water at 14°, in 90 parts of alcohol of sp. gr. 0·85, and in 100 parts of absolute alcohol. Insoluble in ether (Baup).

| | | | Baup. | |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | ................................... | 308 | ........ | 64·42 | |
| 2 $SO^3$ | ................................... | 80 | ........ | 16·73 | ........ 17·24 |
| 2 HO | ................................... | 18 | ........ | 3·76 | |
| 8 aq. | ................................... | 72 | ........ | 15·09 | ........ 15·52 |

| $C^{40}N^2H^{24}O^2,2(HO,SO^3) + 8$ aq. .... | 478 | ........ | 100·00 |

*Iodate of Cinchonine.* — Iodic acid does not precipitate hydrochlorate of cinchonine (v. Planta). — The salt is obtained from aqueous iodic acid and cinchonine. Very delicate white needles, which explode violently at 120° (Serullas, *Ann. Chim. Phys.* 45, 274, Regnault). Dissolves very easily in water, but not in alcohol (Pelletier). From a moderately strong solution (also from the chlorate) aqueous iodic acid precipitates an acid salt (Serullas).

|        |      | at 105°. |        |          | Regnault. |
|--------|------|----------|--------|----------|-----------|
| 40 C   | .......... | 240  | ......... | 49·58 | ........ | 48·69 |
| 2 N    | .......... | 28   | ........  | 5·78  |          |       |
| 25 H   | .......... | 25   | .......   | 5·16  | ........ | 5·20  |
| 8 O    | .......... | 64   | .......   | 13·24 |          |       |
| I      | .......... | 127  | ......... | 26·24 |          |       |
| C⁴⁰N²H²⁴O²,HO,IO⁵ .... | | 484 | ........ | 100·00 | | |

Contains 56·80 p. c. of cinchonine and 35·07 of iodic acid (Serullas).

*Periodate of Cinchonine.* — Cinchonine neutralises aqueous periodic acid only partially ; on evaporation in a vacuum, the solution deposits a resin, in which crystals are afterwards formed. The crystals soon decompose, with formation of iodic acid. — On adding an alcoholic solution of periodic acid to alcoholic cinchonine, and carefully evaporating the neutral liquid, short prisms are obtained, which turn yellow in the air and then contain iodic acid, and at last hydriodic acid (Langlois, *N. Ann. Chim. Phys.* 34, 257 ; *Ann. Pharm.* 83, 153).

*Hydriodate of Cinchonine.* — Iodide of potassium throws down from hydrochlorate of cinchonine, a white powder which becomes crystalline on standing (v. Planta). The salt is deposited from the slightly warmed solution, on cooling, partly in the form of a pale-yellow oil which quickly solidifies in a crystalline mass, and partly in delicate white crystals containing the same proportion of water (Hesse). Long, thick, colourless prisms (Herapath). Its taste is at first slight, but afterwards bitter and metallic. Dissolves less freely than the hydrochlorate (Regnault) in cold water, and crystallises from hot water in needles having a pearly lustre (Pelletier). — Gives off 4·34 p. c. of water at 140°, and then contains 30·68 p. c. of iodine (calc. 29·13 p. c. I) (Regnault). Schwabe obtained from sulphate of betacinchonine and iodide of barium, oblique prisms containing only 1 at. of water, easily soluble in water and alcohol.

|            |                   |     |        |       |        | Hesse. |
|------------|-------------------|-----|--------|-------|--------|--------|
| C⁴⁰N²H²⁴O² | .................. | 308 | ...... | 67·87 |        |        |
| HI         | .................. | 128 | ...... | 28·19 | ...... | 28·43  |
| 2 aq.      | .................. | 18  | ...... | 3·94  | ...... | 4·05   |
| C⁴⁰N²H²⁴O²,HI + 2 aq. .... | | 454 | ...... | 100·00 | | |

*Chlorate of Cinchonine.* — Very white, loose scales and prisms, less fusible than the quinine-salt, and easily decomposible (Serullas, *Ann. Chim. Phys.* 45, 278).

|            |                   |       |        |       |        | Serullas. |
|------------|-------------------|-------|--------|-------|--------|-----------|
| C⁴⁰N²H²⁴O² | .................. | 308   | ...... | 76·71 | ...... | 76·00     |
| ClO⁵       | .................. | 75·5  | ...... | 18·80 | ...... | 18·40     |
| 2 HO       | .................. | 18    | ...... | 4·49  |        |           |
| C⁴⁰N²H²⁴O²,HO,ClO⁵ + aq. .... | | 401·5 | ...... | 100·00 | | |

*Perchlorate of Cinchonine.* — Obtained by precipitating perchlorate of baryta with sulphate of cinchonine and evaporating the filtrate. — Large, highly lustrous prisms, permanent in the air (Bödeker). — Rhombic prisms with perpendicular truncation of the oblique lateral edges *b*, and an oblique end-face *c*, resting on the obtuse prismatic edge, and unequally inclined to the two prismatic faces. The face parallel to this is wanting at the opposite end, and instead of it there occurs a face standing to it in the relation of right to left. — $p : p' = 125° \ 46'$ and $54° \ 14'$; $p : b = 117° \ 7'$; $p : c = 123° \ 46'$; $p' : c = 122° \ 37'$; $b : c = 91° \ 6'$. Cleavable parallel to *b* (Dauber, *Ann. Pharm.* 71, 66). Exhibits fine dichroïsm of blue and yellow, even in very dilute acid solutions. — Melts at 160°, losing water of crystallisation, amounting to 3·57 p. c. of the salt dried at 30°; and explodes with flame when more strongly heated. — Dissolves easily in water and alcohol (Bödeker, *Ann. Pharm.* 71, 59).

|  | | Crystals. | | | | Bodeker. |
|---|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2,2HO$ | ...................... | 326 | ........ | 61·86 | ........ | 60·51 |
| 2 ClO⁷ | .... ................. | 183 | ........ | 34·72 | ........ | 35·41 |
| 2 HO | ................ ........ | 18 | ........ | 3·42 | .... .... | 3·57 |
| $C^{40}N^2H^{24}O^2,2ClHO^8 + 2$ aq. | .... | 527 | ........ | 100·00 | ........ | 99·49 |

*Hydrochlorate of Cinchonine.* — A. *Mono-acid.* — Formed with hydrochloric acid and excess of cinchonine. Needles, fusible below 100° (Pelletier & Caventou). Right prismatic; *t* and *m* (*fig.* 78), form a quadratic prism, bevelled above and below by *l*. Angle *l* : *l* above $= 126°$; $l : t = 116·75°$ (Lösche). The same form was observed also by Hesse. — Retains its lustre in the air, but effloresces easily in the desiccator; loses its water of crystallisation at 100°, and melts above 130°. Sp. gr. = 1·2342 (Hesse). Exerts a right-handed action on polarised light; $[\alpha] \ r = 139·5°$ (Bouchardat). — The salt, with 4 at. water dissolves in 24 parts of water at 10° (Hesse); in 24 parts at 18·75° (Abl); in 22 parts of cold, and in 3·2 parts of hot water (Schwabe). It dissolves in 1·3 parts of alcohol of sp. gr. 0·85 at 16° (Hesse); in 1 part of cold, and ½ part of boiling alcohol (Schwabe). Soluble in 550 parts of ether (Schwabe); in 273 parts of ether of sp. gr. 0·7305 at 15° (Hesse).

|  | | Crystals. | | | Schwabe. | | Hesse. |
|---|---|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | ................ .... ... | 308·0 | ........ | 80·95 | | | |
| HCl | ...................... | 36·5 | ........ | 9·59 | ........ | 9·83 | ........ 9·67 |
| 4 aq. | ...................... | 36·0 | ........ | 9·46 | ........ | 9·49 | ........ 9·47 |
| $C^{40}N^2H^{24}O^2,HCl + 4$ aq. | .... | 380·5 | ........ | 100·00 | | | |

|  | | Dried. | | | | Hesse. |
|---|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | ... ......... | 308·0 | ........ | 89·46 | ........ | 89·4 |
| HCl | ............ | 36·5 | .... .... | 10·54 | ........ | 10·6 |
| $C^{40}N^2H^{24}O^2$ HCl | .... | 344·5 | ........ | 100·00 | ........ | 100·0 |

B. *Bi-acid.* 100 parts of cinchonine take up 22·7 parts of hydrochloric acid (Liebig); when exposed to a stream of hydrochloric acid gas, and afterwards to dry air of 165°, they retain 22·6 parts of hydrochloric acid (2 at. = 23·6 p. c.). The solution of the salt in water yields a strongly acid gum (Regnault). On evaporating cinchonine

with excess of hydrochloric acid, dissolving the residue in weak alcohol, and allowing the solution to evaporate spontaneously, fine tables are obtained, which have an acid reaction, and are easily soluble in water, but less freely in alcohol. Right prismatic. Right rhombic prisms, *u*, *u*, with the base *p*; the acute lateral edges replaced by *i* (fig. 80); tabular from predominance of *p*. Angle $u : u = 101°$; $p : i = 137$ to $138°$ (Laurent). To this belong also the crystals obtained by Hahn; rhombic prisms *y* (fig. 53) having the obtuse lateral edge perpendicularly truncated by *p*, which is perpendicular to the base *t*. Angle $y : y = 30°$, $y : p = 165°$ (Hahn). Also Laurent's salt with the macrodiagonal three times as long (Guthe).

|  | Crystals. |  |  |  | Laurent. | Gössmann. |
|---|---|---|---|---|---|---|
| 40 C | 240 | | 62·99 | | 62·00 | |
| 2 N | 28 | | 7·34 | | | |
| 26 H | 26 | | 6·82 | | 6·66 | |
| 2 O | 16 | | 4·20 | | | |
| 2 Cl | 71 | | 18·65 | | 19·35 | 19·3 |
| $C^{40}N^2H^{24}O^2,2HCl$ | 381 | | 100·00 | | | |

*Hydrofluate of Cinchonine.* — By evaporating cinchonine with excess of hydrofluoric or hydrofluosilicic acid, a strongly acid varnish is obtained (Serullas, *Ann. Chim. Phys.* 45, 282). Cinchonine dissolves freely in dilute hydrofluoric acid; on concentrating the solution by evaporation, colourless right rhombic prisms with four-sided pyramids are obtained. A solution in weak alcohol yields very fine crystals; the solution in stronger alcohol, when almost completely evaporated, yields only needles and a viscid syrup. — The crystals lose 2·81 p. c. of water at 100° (1 at. = 2·52 p. c. HO), becoming milk-white, and on further heating, purple-red, after which they give off a red sublimate and hydrofluoric acid, and carbonise (Elderhorst, *Ann. Pharm.* 74, 80).

|  |  | at 100°. |  |  | Elderhorst. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | 308 | | 88·51 | | 87·52 |
| 2 HF | 40 | | 11·49 | | |
| $C^{40}N^2H^{24}O^2, 2HF$ | 348 | | 100·00 | | |

*Nitrate of Cinchonine.* — A solution of the salt, obtained by double decomposition, or by saturating very dilute nitric acid with cinchonine, deposits, on evaporation, oily drops, which cool to a waxy solid, and become converted into crystals when kept under water. — Large monoclinic twin-crystals, often an inch long (Hesse). According to Pelletier & Caventou, oblique rectangular prisms, easily cleavable parallel to two side-faces, and having on these faces a pearly lustre. According to Lösche, flat oblique-prismatic crystals, bevelled at the ends by two faces forming a very obtuse angle. — Exerts a right-handed action on polarised light; $[\alpha]r = 172°\ 48'$ (Bouchardat). — Permanent in the air (Schwabe). Loses at 100°, on an average, 2·57 p. c. of water (1 at. = 2·37 p. c. HO). The hydrated salt dissolves in 26·4 parts of water at 12°, and freely in water at 40°; the solution heated to boiling deposits the salt in the form of an oil on cooling (Hesse).

Cinchonine is not precipitated by excess of *fluosilicic alcohol* (xv, 437) (Knop); *phosphomolybdic acid* (xiii, 164) precipitates it whitish-yellow (Sonnenschein).

*Phosphantimonic acid* (xiv, 227) throws down bluish-white flocks from a solution containing $\frac{1}{1000}$th of cinchonine (Schulze).

*Chromate of Cinchonine.* — By double decomposition in neutral or acid solutions a bi-acid salt is obtained (André). Warm aqueous hydrochlorate of cinchonine becomes turbid on dropping into it a solution of bichromate of potash, and afterwards deposits small ochre-yellow prisms (Hesse), orange-yellow needles (André), or at too high a temperature, or on too hasty addition of the bichromate, a resin, which does not crystallise (Hesse). A similar observation was made by Elderhorst (*Ann. Pharm.* 74, 80). The precipitate, amorphous at first, becomes crystalline on standing (Seligsohn). Decomposed by exposure to light in the moist state, but not after drying (Hesse). Decomposes at 60° (André), and carbonises at 100°, glowing on exposure to the air (Hesse). Dissolves in 80 parts of boiling water.

|  | *Dried over oil of vitriol.* |  |  | Hesse. |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | 308 | 73·86 | | 74·00 |
| 2 $CrO^3$ | 100 | 23·98 | | 24·05 |
| HO | 9 | 2·16 | | |
| $C^{40}N^2H^{24}O^2,HO,2CrO^3$ | 417 | 100·00 | | |

*Arseniate of Cinchonine.* — *Bibasic.* — Formed from hydrochlorate of cinchonine and arseniate of potash. Long white prisms, very easily soluble in water. Loses its water of crystallisation at 100° (Hesse).

|  |  |  |  | Hesse. |
|---|---|---|---|---|
| 2 $C^{40}N^2H^{24}O^2$ | 616 | 63·24 | | |
| $AsO^5,3HO$ | 142 | 14·59 | | |
| 24 aq. | 216 | 22·17 | | 21·71 |
| $2C^{40}N^2H^{24}O^2,3HO,AsO^5 + 24$ aq. | 974 | 100·00 | | |

*Chlorocadmiate of Cinchonine.* — $C^{40}N^2H^{24}O^2,HCl,CdCl + aq.$ By mixing hydrochlorate of cinchonine and chloride of cadmium, a stiff mass is obtained, which becomes transformed into large crystals (Galletly, *Pharm. Centr.* 1856, 697; *N. Edin. Phil. J.* 4, 94).

*Chlorostannite of Cinchonine.* — Hydrochlorate of cinchonine throws down from a solution of protochloride of tin containing hydrochloric acid, a pale-yellow oil, which afterwards solidifies. The supernatant liquid deposits heavy, pale-yellow prisms, melting at 100° to a yellowish oil, which solidifies to a brittle mass. Contains, after drying at 100°, 27·65 p. c. Cl, rather more than is required by the formula $C^{40}N^2H^{24}O^2,2HCl, 2SnCl$ (calc. 24·93 Cl), the excess being derived from adhering hydrochloric acid. Cannot be recrystallised (Hesse).

Mixed solutions of *ferric sulphate* and sulphate of cinchonine do not yield a double salt (Will, *Ann. Pharm.* 42, 111).

*Iodomercurate of Cinchonine.* — Iodomercurate of potassium throws down from hydriodate (or from acetate or hydrochlorate) of cinchonine a white precipitate, which cakes together in hydrochloric acid, without dissolving (v. Planta; Delffs). The precipitate turns sulphur-yellow on drying: it is amorphous, has a faint taste, and when heated melts, gives off iodine, and decomposes. It is nearly insoluble in water and in alcohol (Caillot, *Ann. Chim. Phys.* 42, 265).

|  |  |  |  |  |  | Caillot. |
|---|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | .................... .... | 308 | ........ | 30·25 | | |
| 2 HI | ............................ | 256 | ........ | 25·16 | | |
| 2 HgI | ............................ | 454 | ........ | 44·59 | ........ | 42·67 |

| $C^{40}N^2H^{24}O^2,2HI + 2HgI$ .... | 1018 | ........ | 100·00 |
|---|---|---|---|

Cinchonine [hydrochlorate? (Kr.)], chloride of mercury, and iodide or bromide of potassium yield double salts corresponding to those of morphine (xvi, 433), nearly insoluble in cold and in boiling water, but soluble in almost all proportions in boiling alcohol (Groves).

*Hydriodate of Cinchonine with Chloride of Mercury?* — On adding a solution of mercuric chloride to hydriodate of cinchonine, a white uncrystallisable precipitate, tasting of corrosive sublimate and cinchonine, is produced. The precipitate is decomposed by acetic acid, with formation of red iodide of mercury. It contains an amount of mercury corresponding to 34·91 p. c. HgCl (Caillot, *Ann. Chim. Phys.* 42, 268). Probably either the iodine-compound or a mixture of the iodine and chlorine compounds (Gmelin).

*Chloromercurate of Cinchonine.* — Previously obtained by Caillot, *Ann. Chim. Phys.* 42, 263. Chloride of mercury throws down from hydrochlorate of cinchonine a white powder, easily soluble in hydrochloric acid, and soluble with difficulty in sal-ammoniac (v. Planta). When a solution of hydrochlorate of cinchonine in strong alcohol acidulated with hydrochloric acid, is mixed with an equal quantity of alcoholic chloride of mercury, the mixture quickly solidifies to a mass of crystals. Purification is effected by washing with water, alcohol, and ether-alcohol in succession. Stable at 100°. — Dissolves in water or weak alcohol on heating only. Freely soluble in strong hydrochloric acid (Hinterberger, *Ann. Pharm.* 77, 202). Schwabe obtained the salt in the form of a white, resinous mass.

|  |  | Dried over the water-bath. |  |  | Hinterberger. |  |
|---|---|---|---|---|---|---|
| 40 C | ...................................... | 240 | ........ | 36·62 | ........ | 35·50 |
| 2 N | ...................................... | 28 | ... .... | 4·29 | | |
| 26 H | ...................................... | 26 | ......... | 3·98 | ........ | 3·83 |
| 2 O | ...................................... | 16 | ........ | 2·66 | | |
| 2 Hg | ...................................... | 200 | ........ | 30·67 | ........ | 31·48 |
| 4 Cl | ...................................... | 142 | ........ | 21·78 | ........ | 21·67 |

| $C^{40}N^2H^{24}O^2,2HCl + 2HgCl$.... | 652 | ........ | 100·00 |
|---|---|---|---|

Contains 29·31 p. c. Hg (Caillot). — According to Hinterberger $C^{38}N^2H^{22}O^2,2HCl + 2HgCl$. Hinterberger afterwards regarded the salt as impure, containing Hlasiwetz's cinchotine. He states also that only commercial cinchonine, when in alcoholic solution, solidifies to a crystalline mass with chloride of mercury; and that on recrystallising the cinchonine, the first crop of crystals obtained yields no double salt, even after standing for 24 hours; but on addition of water, the salt is thrown down as a white precipitate, becoming crystalline in the cold (Hinterberger, *Wien. Acad. Ber.* 7, 432; *Ann. Pharm.* 82, 318).

*Chloroplatinate of Cinchonine.* — Bichloride of platinum throws down from alcoholic hydrochlorate of cinchonine, a crystalline precipitate, which is at first almost white or light-yellow. On dissolving it by long boiling with water, it is deposited, first as a whitish powder, and afterwards in fine dark orange-yellow crystals (Hlasiwetz). Pale lemon-yellow precipitate, crystallising from excess of chloride of pla-

tinum in perfect yellow needles (Erdmann). Right prismatic. The faces $y$, $p$, $t$ of fig. 53; the microscopic crystals are prismatic; $y:y$ (over $m$) $= 119°$ (Lösche). $y$ and $p$ (fig. 53), with the octohedron $\alpha$. $y:y = 5°$; $p:y = 120°$ (!); the edge $aa$: $\acute{a}\,\acute{a}$ (fig. 43) $= 123°$ (Hahn). — Loses 2·8 p. c. of water at 180—200° (Laurent). Dissolves in 500 parts of hot water, one-half crystallising on cooling (Duflos). Insoluble in alcohol and ether.

| | | | | | Duflos. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^3$ | 308 | ........ | 42·75 | ........ | 43·43 |
| 2 H | 2 | ........ | 0·28 | | |
| 6 Cl | 213 | ........ | 29·57 | ........ | 29·20 |
| 2 Pt | 197·4 | ........ | 27·40 | ........ | 26·80 |
| $C^{40}N^2H^{24}O^2,2HCl,2PtCl^2$ | 720·4 | ........ | 100·00 | | |

| | | | | | Hlasiwetz. |
|---|---|---|---|---|---|
| 40 C | 240 | ........ | 33·31 | ........ | 33·1 |
| 2 N | 28 | ........ | 3·89 | | |
| 26 H | 26 | ........ | 3·61 | ........ | 3·6 |
| 2 O | 16 | ........ | 2·22 | | |
| 6 Cl | 213 | ........ | 29·57 | | |
| 2 Pt | 197·4 | ........ | 27·40 | ........ | 27·36 |
| $C^{40}N^2H^{24}O^2,2HCl,2PtCl^2$ | 720·4 | ........ | 100·00 | | |

Contains, at 100°, 27·25 p. c. (Laurent), 27·8 p. c. (Gössman), 27·5 p. c. of platinum (Schwabe).

*Chloride of iridium and sodium* throws down from hydrochlorate of cinchonine, a pale-yellow precipitate soluble in hydrochloric acid (v. Planta).

*Terchloride of gold* throws down from solution of cinchonine a sulphur-yellow precipitate, soluble in alcohol, and slightly also in water [and hydrochloric acid (v. Planta)], but insoluble in ether (Larocque & Thibierge, *J. Chim. méd.* 18, 696).

*Hydrocyanate of Cinchonine.* — The precipitate obtained by the double decomposition of hydrochlorate of cinchonine and cyanide of potassium, consists of cinchonine free from hydrocyanic acid (Hesse). Contrary to Schwabe, who regarded the precipitate as hydrocyanate of cinchonine.

*Hydroferrocyanate of Cinchonine.* — Obtained by precipitating alcoholic cinchonine with alcoholic hydroferrocyanic acid. Yellow crystalline precipitate, difficultly soluble in alcohol. — Evolves a large quantity of hydrocyanic acid when heated, the aqueous solution depositing at the same time a white precipitate, which quickly turns blue (Dollfus, *Ann. Pharm.* 65, 212).

| | | | | | Dollfus. |
|---|---|---|---|---|---|
| 52 C | 312 | ........ | 55·71 | ........ | 54·90 |
| 8 N | 112 | ........ | 20·00 | | |
| 32 H | 32 | ........ | 5·72 | ........ | 6·10 |
| 6 O | 48 | ........ | 8·57 | | |
| 2 Fe | 56 | ........ | 10·00 | ........ | 10·30 |
| $C^{40}N^2H^{24}O^2,2Cy^3FeH^2 + 4$ aq. | 560 | ........ | 100·00 | | |

The yellowish-white precipitate produced by ferrocyanide of potas-

sium in solutions of cinchonine free from excess of acid, contains, according to Seligsohn, hydroferrocyanic acid and cinchonine in the same proportions. — The precipitate disappears on slowly warming the liquid, and is deposited again on cooling in golden-yellow, wedge-shaped prisms.  It dissolves in mineral acids, but is insoluble in excess of ferrocyanide of potassium (J. W. Bills, *Sill. Amer. J.* (2) 26, 108; *N. J. Pharm.* 35, 36; *J. pr. Chem.* 75, 484; further: *Schmidt's medic. Jahrb.* 107, No. 7; *Chem. Centr.* 1861, 231).  This precipitate is not formed in perfectly neutral solutions of cinchonine: ferrocyanide of potassium produces therein only a resinous precipitate, or in dilute solutions a milky turbidity; on the subsequent addition of hydrochloric acid, however, long prisms and rhombic tables are formed in the liquid. The same compound is obtained in scales or needles on dropping ferro-cyanide of potassium into a boiling slightly acid solution of a salt of cinchonine, and cooling.  The flocculent precipitate thereby produced is also converted into crystals on standing, though only when pure cinchonine-salts are employed, and not with the commercial lævo-rotatory salts. — The crystals are neutral, intensely bitter, insoluble in alcohol and cold water, and difficultly soluble in warm water.  The more easily formed solution in water acidulated with hydrochloric acid contains hydroferricyanic acid (Seligsohn, *Medicin. Centralzeit.* 30, 129; *Chem. Centr.* 1861, 231).

*Hydroferricyanate of Cinchonine.* — Ferricyanide of potassium, in not too dilute solution, throws down a yellow precipitate from aqueous hydrochlorate of cinchonine. — Lemon-yellow, hard, pointed crystals, stable at 100° when perfectly dry.  The aqueous solution assumes a blue colour on spontaneous evaporation (Dollfus).

|  |  | *at* 100°. |  |  |  | Dollfus. |
|---|---|---|---|---|---|---|
| 52 C | ............................... | 312 | ... ..... | 55·82 | ........ | 55·22 |
| 8 N | ................................ | 112 | ........ | 20·04 |  |  |
| 31 H | ................................ | 31 | ........ | 5·54 | ........ | 5·70 |
| 6 O | ................................ | 48 | ........ | 8·58 |  |  |
| 2 Fe | ............................... | 56 |  | 10·02 | ........ | 10·34 |
| C⁴⁰N²H²⁴O²,Cy⁶Fe²H³ + 4 aq..... | | 559 | ........ | 100·00 | | |

*Cyanide of mercury* throws down from hydriodate of cinchonine a white, curdy precipitate, insoluble in water and alcohol, from which acids separate red iodide of mercury, evolving hydrocyanic acid at the same time.  The precipitate contains an amount of mercury corre-sponding to 33·94 p. c. HgCy (Caillot, *Ann. Chim. Phys.* 42, 269). (C⁴⁰N²H²⁴O²,2HI + 2HgCy requires 30·8 p. c. HgCy). — The precipi-tate produced by mono-acid hydrochlorate of cinchonine in a mixture of cyanide of mercury and bromide of potassium is, according to Caillot, a compound of *cyanide of mercury with hydrobromate of cinchonine* (*J. Pharm.* 17, 356).

*Cyanoplatinate of Cinchonine.* — By the double decomposition of cyanoplatinate of barium and sulphate of cinchonine, sulphate of baryta and bulky colourless needles are obtained.  When heated the needles melt to a red-brown mass, and afterwards carbonise, leaving a residue of platinum.  Anhydrous.  Difficultly soluble in water; more easily soluble in alcohol (C. A. Martius, *Ann. Pharm.* 117, 376). — Cyanoplatinate of potassium precipitates from solutions of cinchonine

the compound $C^{40}N^2H^{24}O^2,HCy,PtCy + 3$ aq., which melts to a violet liquid, and dissolves in hot water (Delffs, *N. Jahrb. Pharm.* 21, 31 ; *N. Repert.* 13, 36).

|  |  |  |  | Martius. |
|---|---|---|---|---|
| $C^{40}N^2H^{25}O^2,2Cy$ ............... | 363 | ........ | 78·62 |  |
| Pt ............... | 98·7 | ...... | 21·38 | ........ 21·38 |
| $C^{40}N^2H^{24}O^2,HCy,PtCy$ .... | 461·7 | ........ | 100·00 |  |

Martius's formula contains 1 at. H. less than the above.

*Hydrosulphocyanate of Cinchonine.* — Sulphocyanide of potassium throws down from acetate (O. Henry, *J. Pharm.* 24, 194) or hydrochlorate of cinchonine (v. Planta) a white curdy precipitate, which rapidly disappears when heated, and is transformed into shining laminæ on standing. The precipitate is insoluble in liquids containing sulphocyanide of potassium, but dissolves in water and easily in alcohol (Lessage, *J. Pharm.* 26, 140).

Hot solutions deposit the salt, on cooling, in very long, thin needles, which effloresce readily in dry air (Schwabe). Microscopic six-sided prisms, mingled with irregular, flattened rectangular prisms (Anderson). — An alcoholic solution of cinchonine is neutralised with not too dilute hydrosulphocyanic acid. Transparent, shining, anhydrous needles, containing 16·97 p. c. of hydrosulphocyanic acid (calc. 16·07 p. c. $CyHS^2$) (Dollfus).

|  |  | at 100°. |  |  | Dollfus. |
|---|---|---|---|---|---|
| 42 C | ............... | 252 | ........ | 68·67 | ........ 67·86 |
| 3 N | ............... | 42 | ........ | 11·44 |  |
| 25 H | ............... | 25 | ........ | 6·79 | ........ 6·63 |
| 2 O | ............... | 16 | ........ | 4·36 |  |
| 2 S | ............... | 32 | ........ | 8·74 |  |
| $C^{40}N^2H^{24}O^2,CyHS^2$ .... | | 367 | ........ | 100·00 |  |

*Formate of Cinchonine.* — Crystallises with difficulty. The solution, evaporated to a syrup, solidifies to a mass of needles (Bonaparte, *J. Chim. méd.* 18, 685).

*Acetate of Cinchonine.* — A neutral solution of cinchonine in acetic acid deposits crystals of cinchonine and becomes acid when heated to 30° or 40° (Hesse). The acid solution yields on evaporation crystalline granules and pellicles, which are no longer acid, and are but slightly soluble in water [cinchonine ? (Kr.)], but ultimately there remains a gummy mass, from which water takes up an acid salt, leaving a neutral salt behind (Pelletier & Caventou). By spontaneous evaporation Schwabe obtained apparently rectangular prisms ($y : y = 114°$ ; $y : m = 123°$), resembling the sulphate, permanent in the air, and easily soluble in water and alcohol. — Mono-acetate of cinchonine turns litmus red and blue at the same time (De Vrij).

*Oxalate of Cinchonine.* — A. *Bibasic.* — Oxalate of ammonia throws down from salts of cinchonine, a white neutral powder, slightly soluble in cold, but more freely soluble in hot water and hot alcohol ; soluble also in excess of aqueous oxalic acid (Pelletier and Caventou). It is obtained from a dilute aqueous solution in large prisms, which dissolve in 104 parts of water at 10°, and lose their water of crystallisation at 130° (Hesse).

| | Air-dried. | | | Hesse. |
|---|---|---|---|---|
| 2 $C^{40}N^2H^{24}O^2$ ............................ | 616 | ........ | 83·03 | |
| $C^4O^6$ ...................... ................... | 72 | ........ | 9·70 | ........ 9·96 |
| 2 HO ...................................... | 18 | ..... .. | 2·42 | |
| 4 aq. ............................ .. ............ | 36 | ........ | 4·85 | ........ 5·11 |
| $2C^{40}N^2H^{24}O^2,C^4H^2O^8 + 4$ aq..... | 742 | ........ | 100·00 | |

B. *Mono-acid.* — Schwabe obtained oxalate of cinchonine in oily drops, changing to tufts of efflorescent crystals. Probably the mono-acid salt.

*Cyanurate of Cinchonine.* — On boiling freshly precipitated cinchonine with a boiling saturated aqueous solution of cyanuric acid and filtering, this salt is deposited in flat rhombic prisms, which lose 17·79 p. c. of water at 100°, or over oil of vitriol, and nothing more at 200° ; when more strongly heated, they evolve vapour smelling of bitter almond oil. — The salt dissolves with difficulty in water, but is insoluble in alcohol and ether (Elderhorst, *Ann. Pharm.* 74, 84).

*Oxalurate of Cinchonine.* — Parabanic acid is saturated, at the boiling heat, with excess of cinchonine. The filtrate dries up to a yellowish transparent mass, which gradually becomes white and crystalline. It is decomposed by cold hydrochloric acid, with separation of oxaluric acid, and by the boiling acid, with formation of oxalic acid (Elderhorst).

*Mellitate of Cinchonine.* — Obtained as a white precipitate on adding alcoholic cinchonine to an alcoholic solution of mellitic acid (Karmrodt, *Ann. Pharm.* 81, 171).

| | | | | Karmrodt. *mean.* |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ ........ ........ | 308 | ........ | 57·46 | |
| 2 $C^8O^6$ ..................... | 192 | ........ | 35·82 | ........ 37·50 |
| 4 HO ............................. | 36 | ........ | 6·72 | |
| $C^{40}N^2H^{24}O^2,2C^5H^2O^8$.... | 536 | ........ | 100·00 | |

*Succinate of Cinchonine.* — Obtained from cinchonine and excess of succinic acid. Long oblique needles, and thick large crystals. Has a strongly acid reaction. Dissolves easily in cold, and more especially in boiling water. Melts at about 100° to a dark-red mass (Hesse).

| | Needles. | | | Hesse. |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ ............................ | 308 | ........ | 67·99 | ........ 67·43 |
| 2 $C^8H^6O^8$ ............................... | 118 | ........ | 26·05 | |
| 3 HO ........................ ............... | 27 | .... .. | 5·96 | ........ 6·51 |
| $C^{40}N^2H^{24}O^2,C^8H^6O^8 + 3$ aq. ... | 453 | ........ | 100·00 | |

The larger crystals lose 4·24 p. c. = 2 at. of water at 100° (Hesse).

*Aspartate of cinchonine* crystallises easily in needles (Plisson, *J. Pharm.* 15, 274).

*Tartrate of Cinchonine.* — Whilst the compounds of tartaric acid and antitartaric acid (dextrotartaric and levotartaric acids, x, 365) with optically inactive substances are identical in every respect, save in the position of the hemihedral faces of their crystals and in their opposite action on polarised light, the compounds of the two acids with optically

active bodies exhibit differences in composition, in solubility, in their behaviour on heating, &c. An optically active substance may form with one of the acids a compound to which there exists no corresponding compound with the other acid (Pasteur).

A. *Dextrotartrate of Cinchonine.* — a. *Neutral.* Precipitated on mixing solutions of cinchonine-salts with alkaline tartrates (Pelletier and Caventou), or on adding neutral tartrate of potash to hydrochlorate of cinchonine (Hesse). A solution of cinchonine in neutral tartrate of potash, in which it dissolves abundantly, deposits this salt in crystalline tufts on cooling (Arppe). — Small crystals, permanent in the air, having an alkaline reaction, and dissolving in 33 parts of water at 16° (Hesse). Loses 4·65 p. c. of water at 110°, and not more at 180°, beyond which it decomposes. The anhydrous salt is electric (Arppe). After dehydration the salt rapidly takes up water again in moist air. Less easily fusible than the mono-acid salt (Hesse).

| | Crystals. | | | Arppe. | Hesse. |
|---|---|---|---|---|---|
| 2 $C^{40}N^2H^{24}O^2$ | 616 | ...... | 77·78 | | |
| $C^8H^6O^{12}$ | 140 | ...... | 17·67 | | |
| 4 aq | 36 | ...... | 4·55 | 4·65 | 4·68 |
| $2C^{40}N^2H^{24}O^2,C^8H^6O^{12} + 4aq.$ | 792 | ...... | 100·00 | | |

b. *Acid.* — When 294 parts of cinchonine are dissolved, together with 132 parts of dextrotartaric acid, in warm water, the solution yields on cooling star-shaped groups of well-formed, highly lustrous crystals : the same salt is obtained also, though less abundantly, with twice the quantity of dextrotartaric acid ; but if not less than four times the quantity of acid is employed, a bi-acid salt is produced. Rhombic prisms $u$, with bevelling faces $n$, resting on the acute lateral edges, and a right rhombic tetrahedron $\alpha$. Angle $u : u = 130°$ 20' about ; $n : u = 127°$ 40' about ; $\alpha : q = 151°$ 13'. See also Hahn's measurements. Exerts a dextro-rotatory action on polarised light. Neutral in alcoholic, acid in aqueous solution (Pasteur).

The air-dried salt gives off 18·8 p. c. of water in a vacuum, and 13·75 to 14 p. c. at 100° [13·6 p. c. at 110° (Hesse)], at which temperature it assumes a faint red colour, becoming darker at 120°, without further loss of weight (Pasteur). The dried salt slowly absorbs water in moist air (Hesse). — Dissolves very slightly in cold [in 101 parts at 16° (Hesse)], freely in hot water, and abundantly in absolute alcohol (Pasteur).

| | Crystals. | | | Pasteur. | Hesse. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | 308 | ...... | 59·23 | | |
| $C^8H^6O^{12}$ | 140 | ...... | 26·92 | | |
| 8aq | 72 | ...... | 13·85 | 13·75 | 13·60 |
| $C^{40}N^2H^{24}O^2,C^8H^6O^{12} + 8aq.$ | 520 | ...... | 100·00 | | |

B. *Antitartrate of Cinchonine.* — Obtained from anti-tartaric acid and cinchonine in the same manner as the corresponding dextrotartrate. When a large excess of acid is employed, very delicate pearly needles of a bi-acid salt are obtained. — Neutral in alcoholic, acid in aqueous solution. Exerts a dextro-rotatory action on polarised light, about ¼th less powerful than the salt A, b. Loses 4·5 p. c. in weight at 100°, and not more at 120° to 140° : at the latter temperature it becomes

coloured only after a considerable time (C$^{40}$N$^2$H$^{24}$O$^2$,C$^8$H$^6$O$^{12}$ + 2aq. requires 3·78 p. c. HO). — Dissolves very slightly in water: the hydrated salt dissolves in 338 parts of absolute alcohol at 19° (Pasteur).

|  |  | *Crystals.* |  |  |  | Pasteur. |
|---|---|---|---|---|---|---|
| 48 C | .......................................... | 288 | ........ | 60·50 | ........ | 59·85 |
| 2 N | .......................................... | 28 | ........ | 5·88 |  |  |
| 32 H | .......................................... | 32 | ........ | 6·72 | ........ | 6·66 |
| 16 O | .... ..................................... | 128 | ........ | 26·90 |  |  |
| C$^{40}$N$^2$H$^{24}$O$^2$,C$^8$H$^6$O$^{12}$ + 2aq ... | | 476 | ........ | 100·00 | | |

When dextrotartrate or antitartrate of cinchonine is heated at gradually increasing temperatures, dextrotartrate or antitartrate of cinchonicine is first formed and is afterwards converted, with loss of water, into a coloured quinoïdine-salt. If the temperature at this point has reached 170°, and is then maintained constant for five or six hours, a part of the dextrotartaric or antitartaric acid is converted into racemic acid, which by a further change is partially converted into inactive tartaric acid, not resolvable into dextrotartaric and lævotartaric acids (Pasteur).

*Tartrate of Cinchonine and Antimony.* — The solution obtained by decomposing sulphate of cinchonine with baryto-antimonic tartrate yields, on spontaneous evaporation, white nodules containing 24·77 p. c. of water of crystallisation and efflorescing rapidly in the air, and afterwards large crystals, which resemble nitrate of cinchonine, and lose 9·95 p. c. of water at 100°. The dried salt contains 26·4 p. c. of antimony, and 47·48 of cinchonine (Hesse). When treated in the same way as quinidine it does not yield a double salt (Stenhouse).

*Croconate and Rhodizonate of cinchonine* are deep-yellow or red amorphous masses, soluble in water and alcohol (Heller).

*Urate of Cinchonine.* — Uric acid is boiled with freshly precipitated cinchonine and a large quantity of water for some time, and the solution is filtered hot. Prisms, amongst which are many twins, resembling harmotome. Over oil of vitriol, or when heated, the transparent crystals become opaque and break up into a white powder, which ultimately assumes a sulphur-yellow colour. They lose 13·73 p. c. of water at 100°, and no more at higher temperatures (8 at. = 13·14 p. c. HO); at 183° they begin to decompose and carbonise (Elderhorst).

|  | *at* 100°. |  |  |  |  |
|---|---|---|---|---|---|
| C$^{40}$N$^2$H$^{24}$O$^2$ | ..................... | 308 | ........ | 64·69 | ........ | 64·89 |
| C$^{10}$N$^4$H$^4$O$^6$ .... . | .................. | 168 | ........ | 35·31 | | |
| C$^{40}$N$^2$H$^{24}$O$^2$,C$^{10}$N$^4$H$^4$O$^6$.... | | 476 | ........ | 100·00 | | |

*Citrate of Cinchonine.* — A solution of the salt prepared in the cold is decomposed on heating, with separation of cinchonine (Hesse).

A. *Terbasic.* — Obtained from hydrochlorate of cinchonine and citrate of potash. By dissolving it in alcohol and leaving the solution to evaporate spontaneously, it is obtained as a colourless oil, which is converted, after some time, into long, concentrically arranged prisms. The crystals dissolve in 48·1 parts of water at 12°. They lose their water at 100° (Hesse).

|  |  |  | | | Hesse. |
|---|---|---|---|---|---|
| 3 $C^{40}N^2H^{24}O^2$ | 924 | ........ | 77·77 | ........ | 77·76 |
| $C^{12}H^8O^{14}$ | 94 | ........ | 16·17 | | |
| 8 HO | 72 | ........ | 6·06 | ........ | 6·21 |
| $3C^{40}N^2H^{24}O^2,C^{12}H^8O^{14} + 8aq$.... | 1090 | ........ | 100·00 | | |

B. *Bibasic.* — Prepared from cinchonine and excess of citric acid. Small prisms, which dissolve in 55·8 parts of water at 15°. Does not take up water from the air after drying (Hesse).

|  |  |  | | | Hesse. |
|---|---|---|---|---|---|
| 2 $C^{40}N^2H^{24}O^2$ | 616 | ........ | 70·00 | ........ | 70·31 |
| $C^{12}H^8O^{14}$ | 94 | ........ | 21·82 | | |
| 8 HO | 72 | ........ | 8·18 | ........ | 8·45 |
| $2C^{40}N^2H^{24}O^2,C^{12}H^8O^{14} + 8aq$ .... | 782 | ........ | 100·00 | | |

*Picrate of Cinchonine.* — Alcoholic picric acid throws down from an alcoholic solution of cinchonine, a yellow precipitate insoluble in acids (Kemp, *Repert.* 71, 164). A warm aqueous solution of hydrochlorate of cinchonine yields with aqueous picric acid, a yellow precipitate resembling iodide of lead, and becoming dense and crystalline on standing. Contains 46·75 p. c. of cinchonine, corresponding to the formula $2C^{40}N^2H^{24}O^2,3C^{12}X^3H^3O^2$ (calc. 47·2 p. c. cinchonine) (Hesse). A solution in water deposits on boiling, oily drops which do not solidify on standing under water for some days (Bonaparte, *J. Chim. méd.* 18, 685).

A strong aqueous solution of *orcin* throws down from bisulphate of cinchonine, oily drops which solidify in dry air and contain orcin and cinchonine (Du Luynes, *Compt. rend.* 57, 162). — *Picrotoxin* forms with cinchonine, a compound resembling that formed with brucine (Pelletier and Couerbe, *Ann. Chim. Phys.* 54, 187).

*Benzoate of Cinchonine.* — Obtained with excess of cinchonine. Deposited from a boiling aqueous solution on cooling, in small star-shaped prisms, which dissolve in 163 parts of water at 15° (O. Hesse).

|  | *Crystallised.* | | | | Hesse. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | 308 | ........ | 71·62 | ........ | 71·25 |
| $C^{14}H^6O^4$ | 122 | ........ | 28·38 | | |
| $C^{40}N^2H^{24}O^2,C^{14}H^6O^4$ .... | 430 | ........ | 100·00 | | |

*Hippurate of Cinchonine.* — The solution obtained by boiling excess of cinchonine with a hot saturated aqueous solution of hippuric acid and filtering, does not crystallise on cooling, but when evaporated to a syrup, solidifies to a transparent, amorphous mass (Elderhorst).

*Gallic acid* does not precipitate sulphate of cinchonine (Pfaff; Bonnet).

*Tannate of Cinchonine.* Tincture or infusion of galls, in small quantity, precipitates from dilute solutions of hydrochlorate of cinchonine, yellowish-white flocks, which disappear on the addition of a drop of hydrochloric acid, but re-appear in the form of a dense precipitate, on adding more hydrochloric acid (v. Planta).

Cinchonine behaves towards cinchona-red (xv, 482) in the same manner as quinine (Henry & Plisson).

*Kinate of Cinchonine.*    Occurs in cinchona-barks, according to Henry & Plisson. Freshly precipitated cinchonine is dissolved in aqueous kinic acid, and the solution is concentrated and left to stand in the air. More distinctly crystalline than the quinine-salt: easily soluble in water, less freely in alcohol (Henry & Plisson, *Ann. Chim. Phys.* 35, 173). The crystals contain 4 at. water: they dissolve in ½ part of water at 15°, and are decomposed by alcohol. A hot alcoholic solution, which reddens litmus, deposits short flat 4- and 6-sided prisms, colourless and shining, permanent for a time in dry air, but ultimately becoming opaque; deliquescent in moist air, and very soluble in water, whereby a little cinchonine is deposited, and an alkaline solution produced (Baup, *Pogg.* 29, 70; *Ann. Pharm.* 6, 12).

*Roccellate of Cinchonine.* — The easily formed solution of 2 at. cinchonine and 1 at. roccellic acid (xvi, 476) in warm alcohol leaves on evaporation an unctuous mass, insoluble in water and ether (Hesse).

Cinchonine behaves in the same manner as quinine towards *oleic acid* and olive oil (Attfield).

Cinchonine dissolves in 140 parts of *alcohol* of sp. gr. 0·852 at 10°, and in 125·7 parts at 20° (Hesse). Dissolves in 600 parts of cold alcohol of 20° B. (Merck), in 126·5 parts of absolute alcohol, and in 115¾ parts of alcohol of 90 p. c. at 15° (Bussy & Guibourt); in 400 parts of 80 p. c. alcohol at 17°, and in 110 parts at the boiling heat (Erdmann); in 173 parts of cold, and in 43 parts of boiling alcohol (Schwabe). Water throws down a crystalline precipitate from the alcoholic solution (Schwabe). A boiling alcoholic solution deposits two-thirds on cooling (Duflos).

Cinchonine dissolves in 371 parts of *ether* of sp. gr. 0·7305 at 20° (Hesse); in 830 parts of ether (Bussy & Guibourt); in 378 parts of ether (Schwabe); in 600 parts of ether at 17°, and in 470 parts of boiling ether (Erdmann). — It dissolves in cold *creosote* and *picamar* (Reichenbach); in 23·2 parts of *chloroform* (M. Pettenkofer); in 40 parts (beta-cinchonine in 268 parts) of chloroform (Schwabe). Riegel found cinchonine insoluble in chloroform. Dissolves to a very small amount in *oil of turpentine* and *fat oils* (Pelletier & Caventou); in 100 parts of *olive oil* (Pettenkofer). According to Schwabe, beta-cinchonine dissolves easily in volatile and fixed oils, but not in *rock oil.*

Cinchonine does not precipitate *gelatin.*


# Cinchonidine.

$$C^{40}N^2H^{24}O^2 = C^{40}N^2H^{22}O^2,H^2.$$
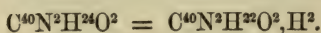
F. L. Winckler. *Repert.* 85, 392; 98, 384; 99, 1; abstr. *Kopp's Jahresber.* 1847 & 1848, 620.

J. A. Buchner. *Repert.* 98, 388.

H. G. Leers. *Ann. Pharm.* 82, 147; abstr. *J. pr. Chem.* 58, 21; *Pharm. Centr.* 1853, 65; *N. Ann. Chim. Phys.* 36, 112; *N. J. Pharm.* 22, 339; *Chem. Gaz.* 1853, 161; *Kopp's Jahresber.* 1852, 533.

Stahlschmidt. *Ann. Pharm.* 90, 218.

Bussy & Guibourt. *N. J. Pharm.* 22, 401 ; *Chem. Centr.* 1853, 205 ; *J. pr. Chem.* 59, 225 ; *Kopp's Jahresber.* 1852, 745.

Pasteur. *N. J. Pharm.* 23, 123 ; *Compt. rend.* 36, 26 ; *J. pr. Chem.* 58, 376 ; *Kopp's Jahresber.* 1853, 472.

Herapath. *Phil. Mag.* [4] 14, 224 ; *J. pr. Chem.* 72, 104 ; *Kopp's Jahresber.* 1857, 405.

Kerner. *Anal. Zeitschrift,* 1, 153.

C. Mann. *Russ. Pharm. Zeitschr.* 2, No. 3 and 4 ; *Pharm. Viertelj.* 13, 245.

F. Koch. *N. Jahrb. Pharm.* 22, 240.

The *Cinchonidine* of Pasteur ; *Chinidine* of Winkler, Leers, Stahlschmidt, and Bussy & Guibourt. Not to be confounded with the *cinchonidine* of Wittstein (xiii, 336 and xvii, 228).

Discovered by Winckler in 1845, but not obtained free from quinine or quinidine, as it was coloured green by chlorine-water and ammonia. It occurs in a bark resembling *China Huamalies,* and also in *China Maracaibo* (Wiggers. 415) (Winckler). A bark described as *China Bogota* contains 2·64 p. c. of cinchona-bases, principally cinchonidine with a little quinine (Leers). It probably occurs in the bark of *Cinchona ovata micrantha* and *cordifolia,* and in Bolivian barks (Howard). In many other cinchona-barks, together with quinine and cinchonine.

According to Kerner, a long-unrecognised cinchona-base, differing from cinchonidine, is found in commerce under that name. It forms shining laminæ and needles ; its hydrochlorate crystallises in hard, long, rhombic prisms : the sulphate is pulverulent, and soluble in 108 parts of water at 15°. Leers also found in Zimmer's cinchonidine, an unknown base richer in carbon.

F. Koch distinguishes Winckler's quinidine from Pasteur's cinchonidine, but does not adequately characterise the two bases. Winckler's quinidine occurs generally in Carthagena bark, together with cinchonidine ; less frequently in Pitayo barks, and never in Calisaya bark. It forms small granules, which do not turn dull in the air, and dissolve abundantly in alcohol and ether-alcohol, but are nearly insoluble in ether. The sulphate forms long transparent needles, harder and less flexible than those of sulphate of quinine, and having a vitreous lustre. The crystals turn brown in sunlight, do not fluoresce when dissolved in sulphuric acid, and give off 20 p. c. of water at 80—100°. The hydrochlorate forms large transparent octahedrons. — Pasteur's cinchonidine occurs to the extent of 1 per cent. in the Carthagena barks, which are scarcely known in commerce (see above). It forms short, six-sided prisms, permanent in the air, and difficultly soluble in alcohol and ether. The sulphate resembles the sulphate of cinchonidine described below (Koch).

Sulphate of cinchonidine is sometimes obtained in the preparation of sulphate of quinine, and on this account it formerly occurred as an admixture in the quinine and quinine-salts of commerce. It is also sold under the name of *Chinidinum sulphuricum.*

*Purification.* 1. Commercial cinchonidine is exhausted with ether, which dissolves out a large quantity of quinine and resin. The undissolved portion is treated with hot alcohol of 80 p. c., and the solution is digested with animal charcoal and allowed to evaporate slowly, whereby coloured crystals are obtained. The crystals are converted

into sulphate, and purified in the same manner as sulphate of quinine, and the sulphate is dissolved in hot water and decomposed by carbonate of soda; the precipitate is washed, dried, and dissolved in alcohol; and the solution is treated with animal charcoal, filtered, and evaporated till it crystallises. In this way colourless crystals are obtained, amounting to $\frac{1}{4}$th of the crude product (Winckler). — 2. Commercial cinchonidine is dissolved in alcohol of 90 p. c , and the solution is left to evaporate in the air, whereupon a yellowish-green resin is first deposited at the edges, and afterwards crystals make their appearance. The crystals are picked out and again dissolved in alcohol, when a second portion of resin is deposited; and this treatment is repeated until the resin is completely removed. The crystals obtained after five or six recrystallisations are triturated and washed with ether until chlorine-water and ammonia no longer indicate the presence of quinine (Leers).

When a solution of 1 part of sulphate of cinchonidine containing quinine in 10 parts of alcohol of 90 p. c. is supersaturated with ammonia, and the solution is filtered from sulphate of ammonia, and warmed with its own weight of water, shining laminæ of cinchonidine are obtained on cooling. The mother-liquor, mixed with more warm water, deposits a further quantity of cinchonidine on cooling, but accompanied by oily drops of quinine (Bussy and Guibourt).

*Properties.* Colourless, highly lustrous, hard prisms, *y, y* (*fig.* 53) of 86° and 94°, with deeply striated faces, including the face *p*, parallel to which the crystals are cleavable. Terminated above by two shining faces *u*, forming an angle of 114° 30′ (Leers). Rectangular or rhombïodal prisms (Bussy & Guibourt). Rectangular four-sided prisms, sometimes perpendicularly truncated, sometimes bevelled with two faces, or terminated by one oblique face. When rapidly crystallised, it forms a scaly powder, consisting of transparent, microscopic rhombic tables (Winckler). A solution in chloroform (or acetic acid) yields on evaporation fine crystalline nodules, which exhibit a black cross and white or coloured rings in polarised light (Herapath). Hard and easily powdered. According to Leers, it is electric when rubbed, but according to Winckler it is not. The anhydrous crystals retain their form and lustre when heated, and melt at 175°, without loss of weight, to a wine-yellow liquid, which solidifies to a whitish-grey crystalline mass on cooling (Leers; Winckler). Less bitter than quinine (Leers). Tastes at first slightly, afterwards intensely bitter (Buchner). Rotates a ray of polarised light to the left : $[\alpha] j = 144\cdot61°$ (Pasteur), $= 142\cdot8°$ (Bouchardat & Boudet); stronger in hydrochloric or sulphuric acid solution (Bouchardat & Boudet, *N. J. Pharm.* 23, 288).

| | According to Pasteur. | | | | According to Leers. | | | | Leers. mean (6). |
|---|---|---|---|---|---|---|---|---|---|
| 40 C | ............ | 240 | .... | 77·92 | 36 C........ ........ | 216 | .... | 76·59 | .... | 76·66 |
| 2 N | ............ | 28 | .... | 9·09 | 2 N ............... | 28 | .... | 9·93 | .... | 9·99 |
| 24 H | ............ | 24 | .... | 7·79 | 22 H............... | 22 | .... | 7·80 | .... | 7·74 |
| 2 O | ............ | 16 | .... | 5·20 | 2 O ... ... ... ... | 16 | .... | 5·68 | .... | 5·61 |
| C⁴⁰N²H²⁴O² ... | | 308 | .... | 100·00 | C³⁶N²H²²O² .... | 282 | .... | 100·00 | .... | 100·00 |

Leers' formula, which agrees with his analyses better than that of Pasteur, is not admissible, if, as Pasteur states, cinchonidine yields cinchonicine when heated, like cinchonine. For this reason Gerhardt (*Traité* 4, 138) gives the preference to

Pasteur's formula, whereas Limpricht (*Lehrb.* 1180) regards Leers and Stahlschmidt's base as different from Pasteur's cinchonidine, and considers the latter body identical with Schwabe's betacinchonine (p. 200). But inasmuch as Pasteur's base exerts a left-handed, and Schwabe's a right-handed action on polarised light, Limpricht's view is obviously erroneous. Moreover Stahlschmidt's analysis of methyl-cinchonidine (p. 233) can scarcely be accepted as evidence of the correctness of Leers's formula, and his analyses of the cinchonine derivatives also gave too little carbon (Kr.).

*Decompositions.* — 1. When *heated* (under the conditions stated under cinchonine) the salts of cinchonidine are converted into salts of cinchonicine (Pasteur). — 2. Fused cinchonidine takes fire when more strongly heated, *burns* with a red smoky flame, evolving an odour of chinoline and bitter almonds, and leaves a little easily combustible charcoal (Winckler; Leers). A slight sublimate is sometimes obtained in a glass tube, and consists, according to Winckler, of unchanged cinchonidine. — 3. Cinchonidine dissolves in *oil of vitriol* and *strong nitric acid*, without colour: the solutions turn brown and decompose when heated (Winckler). On addition of chromate of potash, the solution assumes a pale-yellow colour, as with cinchonine, not dark-yellow, as is the case with quinine (Buchner). — 4. Cinchonidine forms, with *iodine* and sulphuric acid, a compound closely resembling sulphate of iodo-quinine (Herapath). See below. — 5. A solution of cinchonidine in *chlorine-water* is not altered by ammonia (Leers): according to Wittstein, ammonia colours the solution a dirty-yellow, and at the same time throws down grey-white flocks, which dissolve to a wine-yellow liquid in a larger quantity of ammonia. Cinchonidine is not reddened by chlorine-water, ferricyanide of potassium, and ammonia (Mann). — 6. Cinchonidine combines with *iodide of methyl*, forming hydriodate of methyl-cinchonidine (Stahlschmidt). — 7. Yields chinoline (xiii, 243) when heated with *hydrate of potash*.

*Combinations.* Cinchonidine dissolves less freely than quinine in *water* (Winckler); in 2580 parts of water at 17°, and in 1858 parts boiling (Leers).

Cinchonidine dissolves somewhat slowly in *acids*, forming neutral salts. According to Winckler, solutions containing excess of acid are fluorescent, but according to Herapath, very feebly so. The *salts* are either mono- or bi-acid, and for the most part crystallisable. They dissolve in water more easily than the corresponding quinine-salts, and very freely in alcohol, but are nearly insoluble in ether. From aqueous solutions of the salts, ammonia and caustic alkalis, and their carbonates and bicarbonates, throw down white precipitates, which become crystalline on standing, and are (nearly) insoluble in excess of the precipitants (Leers; Winckler). Ammonia in excess dissolves freshly precipitated cinchonidine less easily than quinidine or quinine (Kerner; Mann).

*Phosphate of Cinchonidine.* — Thrown down from the mono-sulphate as a white precipitate, by a slight excess of phosphate of soda. Microscopic, transparent 4-sided prisms, perpendicularly truncated. Loses its water at 100° (Winckler).

|  | *Air-dried.* |  |  |  | Winckler. |
|---|---|---|---|---|---|
| 3 $C^{40}N^2H^{24}O^2$ | 924 | ........ | 69·16 |  |  |
| 2 $PO^5$ | 142 | ........ | 10·63 | ........ | 10·23 |
| 6 HO | 54 | ........ | 4·04 |  |  |
| 24 HO | 216 | ........ | 16·17 | ........ | 17·20 |

$3C^{40}N^2H^{24}O^2,2(PO^5,3HO) + 24aq$ .... 1336 ........ 100·00

Winckler gives no formula.

*Hyposulphite of Cinchonidine.* — A solution of the mono-sulphate mixed with hyposulphite of soda yields, on cooling, long slender needles, difficultly soluble in water, but more easily soluble in alcohol (Leers).

*Sulphate of Cinchonidine.* — A. *Mono-acid.* — Obtained by neutralising dilute sulphuric acid with cinchonidine and evaporating. Radiated groups of long needles, having a silky lustre (Leers). Resembles sulphate of quinine, but appears under the microscope as delicate, transparent, 4-sided needles, perpendicularly truncated (Winckler). The moist sulphate is gelatinous and curdy; when dry it resembles magnesia (Kerner). Dazzling dead-white (Winckler). Neutral (Leers).

Dissolves in 97 parts of cold water (Bussy & Guibourt); in 73 parts of cold, and in 4·2 parts of hot water (Howard); in 95 to 100 parts of water at 15° (Kerner). The salt dried at 110° dissolves in 130 parts of water at 17°, and in 16 parts boiling (Leers). Dissolves in a cold saturated solution of Glauber's salt, but is almost insoluble in aqueous Rochelle salt, so that the filtrate is not rendered turbid by ammonia (Mann). Dissolves very easily (Leers), more freely than sulphate of quinine (Bussy & Guibourt), in alcohol, but is almost insoluble in ether (Leers). — The air-dried salt contains 17·52 p. c. of water, and 9·48 of sulphuric acid (Winckler) ($C^{40}N^2H^{24}O^2,SO^3,HO + 8$ aq. $= 16·94$ p. c. aq., 9·41 $SO^3$).

| *According to Pasteur.* |  |  |  | *According to Leers.* |  |  |  | Leers. |
|---|---|---|---|---|---|---|---|---|
| 40 C | 240 | .... | 67·22 | 36 C | 216 | .... | 65·25 | .... 64·75 |
| 2 N | 28 | .... | 7·84 | 2 N | 28 | .... | 8·46 |  |
| 25 H | 25 | ... | 7·00 | 23 H | 23 | .... | 6·95 | .... 7·05 |
| 3 O | 24 | .... | 6·72 | 3 O | 24 | .... | 7·26 |  |
| $SO^3$ | 40 | .... | 11·22 | $SO^3$ | 40 | .... | 12·08 | .... 12·01 |

$C^{40}N^2H^{24}O^2,SO^3,HO$  357 ... 100·00      $C^{36}N^2H^{22}O^2,SO^3,HO$  331 .... 100·00

B. *Bi-acid.* — Delicate, dull, asbestos-like needles, losing 17·5 p. c. of water at 100°, and 19 p. c. on melting (Winckler).

|  | *Air-dried.* |  |  |  | Winckler. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | 308 | ........ | 62·09 |  |  |
| 2 $SO^3$ | 80 | ........ | 16·13 | ........ | 16·55 |
| 2 HO | 18 | ........ | 3·63 |  |  |
| 10 HO | 90 | ........ | 18·15 | ........ | 17·5 to 19 |

$C^{40}N^2H^{24}O^2,2(SO^3,HO) + 10aq$ .... 496 ........ 100·00

Leers found varying quantities of sulphuric acid, probably on account of the presence of mono-acid salt.

*Chlorate of Cinchonidine.* — Obtained by decomposing the mono-sulphate with chlorate of potash and crystallising the product from

alcohol. Tufts of long white prisms, which melt to a transparent liquid when heated and then explode violently (Leers).

*Hydrochlorate of Cinchonidine.* — A. *Mono-acid.* — Warm aqueous hydrochloric acid is neutralised with cinchonidine, and the solution is left to evaporate spontaneously. The salt forms large rhombic prisms having a vitreous lustre (Leers); nearly regular, thick rhomboïdal octahedrons, whereas the hydrochlorates of all other cinchona-bases crystallise in long needles (Kerner). When dried at 100° it dissolves in 27 parts of water at 170° and very easily in alcohol, but scarcely in ether (Leers).

*According to Pasteur.*

|        |        |       |       |        |
| ------ | ------ | ----- | ----- | ------ |
| 40 C   | ...... | 240   | ..... | 69·67  |
| 2 N    | ...... | 28    | ..... | 8·11   |
| 25 H   | ...... | 25    | ..... | 7·26   |
| 2 O    | ...... | 16    | ..... | 4·64   |
| Cl     | ...... | 35·5  | ..... | 10·32  |

$C^{40}N^2H^{24}O^2,HCl$ ........ 344·5 ............ 100·00

*According to Leers.*

|        |        |       |       |        |        | Leers. |
| ------ | ------ | ----- | ----- | ------ | ------ | ------ |
| 36 C   | ...... | 216   | ..... | 64·19  | ...... | 64·34  |
| 2 N    | ...... | 28    | ..... | 8·32   |        |        |
| 25 H   | ...... | 25    | ..... | 7·43   | ...... | 7·17   |
| 4 O    | ...... | 32    | ..... | 9·52   |        |        |
| Cl     | ...... | 35·5  | ..... | 10·54  | ...... | 10·05  |

$C^{36}N^2H^{22}O^2,HCl + 2aq.$ .... 336·5 ........ 100·00

Leers supposes the salt dried at 100° to contain water, which, however, is not proved.

B. *Bi-acid.* — To the salt A is added as much hydrochloric acid as it contains already, and the mixture is allowed to evaporate spontaneously. Large shining crystals belonging to the oblique prismatic system. *u, i, f* (fig. 85). *u : u′* right and left = 95° ; *i : u* = 98° ; *f : u* = 116° ; *i : f* = 127° about. From predominance of *i* and *f* the crystals have the appearance of horizontal rhombic prisms (Kopp). After drying over oil of vitriol, the salt loses 5·8 p. c. of water at 100° (2 at. ? = 4·5 p. c. HO). Dissolves very easily in water and alcohol (Leers).

*at 100°.*

|        |        |       |       |        |        | Leers. |
| ------ | ------ | ----- | ----- | ------ | ------ | ------ |
| 36 C   | ...... | 216   | ..... | 57·93  | ...... | 58·30  |
| 2 N    | ...... | 28    | ..... | 7·52   |        |        |
| 26 H   | ...... | 26    | ..... | 6·97   | ...... | 7·12   |
| 4 O    | ...... | 32    | ..... | 8·59   |        |        |
| 2 Cl   | ...... | 71    | ..... | 18·99  | ...... | 18·98  |

$C^{36}N^2H^{22}O^2,2HCl + 2HO$ .... 373 ........ 100·00

In this salt also the amount of water is not definitely established.

*Hydrofluate of Cinchonidine.* — Cinchonidine suspended in water is dissolved by hydrofluoric acid vapour to an opalescent liquid, which on spontaneous evaporation deposits white silky needles, easily soluble in water (Leers).

*Nitrate of Cinchonidine.* — Fine large warty crusts, having the appearance of enamel, obtained by neutralising nitric acid with cinchoni-

dine and leaving the solution to evaporate. Dissolves very easily in water (Leers).

*Iodomercurate of potassium* throws down a yellowish-white amorphous precipitate, even from very dilute solutions of cinchonidine (Delffs).

*Chloromercurate of Cinchonidine.* — Obtained by adding a warm alcoholic solution of cinchonidine acidulated with hydrochloric acid, to an equal quantity of alcoholic mercuric chloride, and leaving the mixture to cool. — Small pearly scales, which do not lose water at 100° after drying over oil of vitriol. Dissolves with difficulty in cold water (Leers).

*According to Pasteur.*

| | | | |
|---|---|---|---|
| 40 C | ..... | 240 | ..... | 36·81 |
| 2 N | ..... | 28 | ..... | 4·29 |
| 26 H | ..... | 26 | ..... | 3·98 |
| 2 O | ..... | 16 | ..... | 2·46 |
| 4 Cl | ..... | 142 | ..... | 21·78 |
| 2 Hg | ..... | 200 | ..... | 30·68 |

C⁴⁰N²H²⁴O²,2HCl,2HgCl .... 652 ..... 100·00

*According to Leers.* Leers.

| | | | | |
|---|---|---|---|---|
| 36 C | ..... | 216 | ..... | 34·51 | ..... 34·77 |
| 2 N | ..... | 28 | ..... | 4·47 | |
| 24 H | ..... | 24 | ..... | 3·83 | ..... 4·01 |
| 2 O | ..... | 16 | ..... | 2·56 | |
| 4 Cl | ..... | 142 | ..... | 22·68 | ..... 22·46 |
| 2 Hg | ..... | 200 | ..... | 31·95 | ..... 31·95 |

C³⁶N²H²²O²,2HCl,2HgCl .... 626 ..... 100·00

Cinchonidine-salts form a white precipitate with *nitrate of silver;* bright-yellow with *terchloride of gold;* brown with *chloride of palladium* (Leers).

*Chloroplatinate of Cinchonidine.* — Orange-yellow precipitate, containing, on an average, after washing with acidulated water and drying at 110°, 27·11 p. c. platinum (Leers).

*According to Pasteur.*

| | | | |
|---|---|---|---|
| C⁴⁰N²H²⁴O² | ..... | 308 | ..... | 42·76 |
| 2 HCl,4Cl | ..... | 215 | ..... | 29·84 |
| 2 Pt | ..... | 197·4 | ..... | 27·40 |

C⁴⁰N²H²⁴O²,2HCl,2PtCl² .... 720·4 ..... 100·00

*According to Leers.* Leers. Winckler.

| | | | | | |
|---|---|---|---|---|---|
| C³⁶H²H²²O² | ..... | 282 | ..... | 40·61 | | |
| 2 HCl,4Cl | ..... | 215 | ..... | 30·96 | | |
| 2 Pt | ..... | 197·4 | ..... | 28·43 | ..... 27·11 | ..... 26·37 |

C³⁶N²H²²O²,2HCl,2PtCl² .... 694·4 ..... 100·00

Leers supposes the salt to contain 4 at. of water which is not shown by the analysis.

Cinchonidine is not precipitated by *platinocyanide of potassium* (Delffs).

*Sulphocyanide of ammonium* gives a white precipitate with salts of cinchonidine.

*Formate of cinchonidine* forms long silky needles, easily soluble in water (Leers).

*Acetate of Cinchonidine.* — Obtained by dissolving cinchonidine in warm dilute acetic acid, and cooling. Fine silky needles, which give off acid on drying, and are very sparingly soluble in water. The mother-liquor yields other needles, more easily soluble in water (Leers).

*Oxalate of Cinchonidine.* — Alcoholic oxalic acid, neutralised with cinchonidine, crystallises on cooling in long silky needles, very sparingly soluble in water. The mother-liquor yields, by spontaneous evaporation, dull white nodules, more easily soluble (Leers).

*Butyrate of Cinchonidine.* — Large porcelain-like nodules and crusts, having an odour of butyric acid. Easily soluble (Leers).

*Tartrate of Cinchonidine.* — A. A neutral solution of cinchonidine in tartaric acid deposits first slender needles having a vitreous lustre, and afterwards dull white nodules. — B. A hot acid solution yields, on cooling, small pearly needles, very difficultly soluble in water (Leers). The dextrotartrate and antitartrate of cinchonidine undergo, when heated, the transformation into cinchonicine-salts described under cinchonine (p. 217) (Pasteur).

Cinchonidine when boiled with *tartar-emetic*, does not yield a double salt corresponding to that obtained with cinchonine (Stenhouse).

*Valerate of Cinchonidine.* — Warty crusts smelling of valerianic acid. Turns brown and decomposes on evaporation over the water-bath (Leers).

*Citrate of Cinchonidine.* — The neutral solution yields small needles, sparingly soluble in water (Leers).

*Hippurate of Cinchonidine.* — Hot alcoholic hippuric acid is neutralised with cinchonidine and left to cool. Long, silky, fern-like laminæ, easily soluble in water and alcohol (Leers).

*Kinate of Cinchonidine.* — White silky needles, easily soluble in water and alcohol (Leers).

The salts of cinchonidine are precipitated of a dirty-yellow colour by *tannic* acid (Leers). — Cinchonidine behaves towards *oleic acid* and olive oil in the same manner as quinine (Attfield).

Cinchonidine dissolves slowly in cold *alcohol* of 80 p. c. to nearly the same extent as quinine, and in all proportions in boiling alcohol. Water turns the solution milky, and after some days throws down a crystalline powder (Winckler). Dissolves in 12 parts of alcohol of sp. gr. 0·835 at 17° (Leers); in 105 parts of alcohol of 90 p. c. at 15° (Bussy & Guibourt).

Soluble in 144 parts of *ether* at 12·5° (Winckler); in 143 parts of sp. gr. 0·728 at 17° (Leers); in 158·5 parts of ether (Bussy & Guibourt).

*Appendix to Cinchonidine.*

# 1. Wittstein's Cinchonidine.

Already treated of as $C^{18}NH^{10}O$ (xiii, 336). Resembles most nearly the cinchonidine of Pasteur, from which, however, it differs, according to Herapath, in the properties of its compound with iodine and sulphuric acid. Cinchonidine prepared by Wittstein was examined by De Vrij (*Haaxmann's Tijdschrift vor Wetensch. Pharm.* [2] 4 Jahrg.; *Kopp's Jahresber.* 1857, 405); it was coloured and contained sulphuric acid, and was found to be a mixture of Pasteur's lævo-rotatory cinchonidine, dextro-rotatory cinchonine, and probably a third base. Afterwards a body prepared by Howard, and recognised by Wittstein as cinchonidine, was found to have a lævo-rotatory action on polarised light, and was identical with Pasteur's cinchonidine (De Vrij, *N. J. Pharm.* 31, 187). The description of the salts given below seems to show also that the substance investigated by Crawfurd (*Pharm. Viertelj.* 7, 535), if it belonged to the known cinchona-bases, may be regarded as identical with Pasteur's cinchonidine.

*Sulphate of Cinchonidine.* — a. *Mono-acid.* Prepared with excess of cinchonidine and dilute acid. Radiate groups of pearly needles, which in concentrated solutions are matted together in a jelly, and dry up to an apparently amorphous, curdy mass. Neutral. Dissolves in 94·6 parts of water at 10°; in its own weight of boiling water; in 47·9 parts of alcohol at 10°; and 1½ parts of boiling alcohol; in 18 parts of ether of sp. gr. 0·74 at 10° (Crawfurd).

| | | | | | | Crawfurd. |
|---|---|---|---|---|---|---|
| $C^{36}N^2H^{20}O^2$ | | 280 | ...... | 78·66 | ...... | 76·36 |
| $SO^3$ | | 40 | ...... | 11·23 | ...... | 11·66 |
| 4 HO | | 36 | ...... | 10·11 | ...... | 11·98 |
| $C^{36}N^2H^{20}O^2,HO,SO^3 + 3aq.$ | .... | 356 | ...... | 100·00 | ...... | 100·00 |

b. *Bi-acid.* — Acid amorphous gum, easily soluble in water and in alcohol (Crawfurd).

*Hydrochlorate of Cinchonidine.* — Formed by warming dilute hydrochloric acid with cinchonidine till the solution acquires a neutral reaction. — Colourless octohedrons, turning cloudy at 80° from loss of water. Dissolves in 27·76 parts of water at 10°, and in ½ part of boiling water; in 5·37 parts of alcohol at 10°, and in ½ part of boiling alcohol in 10·5 parts of ether of sp. gr. 0·74 at 10° (Crawfurd).

| | | | | | | Crawfurd. |
|---|---|---|---|---|---|---|
| $C^{36}N^2H^{20}O^2$ | | 280 | ...... | 58·45 | ...... | 58·36 |
| 2 HCl | | 73 | ...... | 15·24 | ...... | 15·18 |
| 14 HO | | 126 | ...... | 26·31 | ...... | 26·46 |
| $C^{36}N^2H^{20}O^2,2HCl + 14aq.$ | ..... | 479 | ...... | 100·00 | ...... | 100·00 |

*Nitrate of Cinchonidine.* — a. *Mono-acid.* — On neutralising warm dilute nitric acid completely with cinchonidine, there separates an oily layer, which solidifies to a crystalline mass, whilst colourless rhombohedrons containing a larger proportion of water crystallise from the liquid beneath. — Neutral. Very bitter. The salt containing 8 atoms

of water dissolves in 73·52 parts of water at 10°, and in its own weight of boiling water (Crawfurd).

| Oily layer. | | | | | Crawfurd. |
|---|---|---|---|---|---|
| $C^{36}N^2H^{20}O^2$ | 280 | ........ | 70·51 | ........ | 70·08 |
| $NO^5$ | 54 | ........ | 13·60 | ........ | 13·52 |
| 7 HO | 63 | ........ | 15·89 | ........ | 16·40 |
| $C^{36}N^2H^{20}O^2,HO,NO^5 + 6aq.$ .... | 397 | ........ | 100·00 | ........ | 100·00 |

| Rhombohedrons. | | | | | Crawfurd. |
|---|---|---|---|---|---|
| $C^{36}N^2H^{20}O^2$ | 280 | ........ | 67·47 | ........ | 67·90 |
| $NO^5$ | 54 | ........ | 13·01 | ........ | 13·09 |
| 9 HO | 81 | ........ | 19·52 | ........ | 19·01 |
| $C^{36}N^2H^{20}O^2,HO,NO^5, + 8aq.$ .... | 415 | ........ | 100·00 | ........ | 100·00 |

b. *Bi-acid.* — Acid, amorphous gum, easily soluble in water and in alcohol (Crawfurd).

*Acetate of Cinchonidine.* — White, crystalline powder, bitter and neutral. Dissolves easily in water and alcohol, less freely in ether (Crawfurd).

| | | | | | Crawfurd. |
|---|---|---|---|---|---|
| $C^{36}N^2H^{20}O^2$ | 280 | ........ | 72·73 | ........ | 72·97 |
| $C^4H^3O^3$ | 51 | ........ | 13·25 | ........ | 13·10 |
| 6 HO | 54 | ........ | 14·02 | ........ | 13·93 |
| $C^{36}N^2H^{20}O^2,C^4H^4O^4 + 5aq.$ .... | 385 | ........ | 100·00 | ........ | 100·00 |

*Dextrotartrate of Cinchonidine.* — Precipitated on mixing alcoholic solutions of the acid and cinchonidine. According to Crawfurd $2C^{36}N^2H^{20}O^2,C^8H^4O^{10}$. Nearly insoluble in water, alcohol, and ether (Crawfurd).

# 2. Pseudoquinine.

MENGARDUQUE. *N. J. Pharm.* 14, 343; *Compt. rend.* 27, 219; *J. pr. Chem.* 45, 356; *Kopp's Jahresber.* 1847 & 1848, 621.

From the extract of an unknown cinchona-bark, which yielded neither quinine nor cinchonidine. — The extract, boiled with water and an equal quantity of sal-ammoniac till the evolution of ammonia ceased, deposited on cooling a large quantity of a brown syrup, after which aqueous ammonia added to the supernatant liquid threw down yellow flocks. These flocks were dried and treated with cold ether, in which a large proportion dissolved; and on evaporating the ethereal solution the pseudoquinine remained in the form of a white powder.

Tasteless, irregular prisms, melting when heated. Contains, on an average, 76·60 p. c. C., 10·3 N., 8·15 H., and 4·95 O.

Pseudoquinine, when *heated*, burns with a blue flame and leaves no residue. — Its solution in *chlorine-water* is coloured reddish-yellow by ammonia.

Insoluble in *water*, but soluble even in very dilute *acids*, including

the organic acids. The salts are precipitated by ammonia, potash, and soda, but pseudoquinine expels ammonia from sal-ammoniac on boiling. — A neutral solution may be formed with *sulphuric acid*: it tastes slightly bitter, and when concentrated yields fine flat prisms.

The *hydrochlorate* does not crystallise.

Pseudoquinine dissolves in *alcohol*, especially when hot, and is precipitated from the solution by water. Boiling *ether* dissolves only traces of it.

*Conjugated Compounds of Cinchonine and Cinchonidine, and Compounds derived therefrom.*

## Cinchonicine.

$$C^{40}N^2H^{24}O^2 = C^{40}N^2H^{22}O^2,H^2.$$
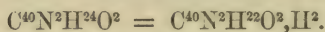
PASTEUR. *Compt. rend.* 37, 110; *N. J. Pharm.* 24, 161; *J. pr. Chem.* 60, 129; *Ann. Pharm.* 88, 209; *Chem. Gaz.* 1853, 321; *Kopp's Jahresber.* 1853, 473.

*Formation.* By heating salts of cinchonine or cinchonidine to a temperature at which they melt without undergoing complete decomposition, both bases are converted into one and the same isomeric product, cinchonicine.

*Preparation.* Sulphate of cinchonine, with the addition of a little water and sulphuric acid, is heated to 120° or 130° for three or four hours, whereby a slightly coloured product is obtained.

*Properties.* Cinchonicine is precipitated from its solutions in the form of a semifluid resin. It is very bitter and antifebrile. Exerts a slight dextrorotatory action on polarised light.

Cinchonicine is insoluble in *water*. — It combines with *carbonic* and other *acids*, and expels ammonia from the salts of that base. — A solution of cinchonicine in aqueous *racemic acid* deposits, at first, crystals consisting principally of antitartrate of cinchonicine, whilst the mother-liquid contains the cinchonicine salt of dextrotartaric acid. The racemic acid is, therefore, split up in the manner described at page 366, vol. x.

Cinchonicine dissolves very easily in *alcohol* and *ether*.

## Hydrocinchonine.

$$C^{40}N^2H^{26}O^4 = C^{40}N^2H^{24}O^4,H^2.$$
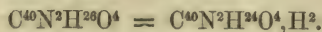
SCHÜTZENBERGER. *Compt. rend.* 46, 1067; *J. pr. Chem.* 74, 227; *Ann. Pharm.* 108, 347; *Kopp's Jahresber*, 1858, 370.

*Hydrate de cinchonine.* Contains $H^2O^2$ more than cinchonine.

Hydrogen is evolved in a mixture of sulphuric acid and sulphate of cinchonine by the addition of zinc; and after some time the solution is precipitated by excess of ammonia. The oxide of zinc redissolves in the ammoniacal liquid, and there remains undissolved a tenacious substance, which is purified by dissolving it in alcohol and evaporating the filtered solution.

Amorphous, not bitter resin, obtained in the anhydrous state by drying at 150°. — Hydrocinchonine dried at 120° contains 2 at. water, one of which is expelled at 140°.

| | | | at 140°. | | | Schützenberger. |
|---|---|---|---|---|---|---|
| 40 | C | ......... | 240 | ......... | 71·64 | ......... 71·56 |
| 2 | N | ......... | 28 | ......... | 8·35 | |
| 27 | H | ......... | 27 | ......... | 8·06 | ......... 8·04 |
| 5 | O | ......... | 40 | ......... | 11·95 | |
| $C^{40}N^2H^{26}O^4,HO$ | | .... | 335 | ......... | 100·00 | |

| | | | at 120°. | | | Schützenberger. |
|---|---|---|---|---|---|---|
| 40 | C | ......... | 240 | ......... | 69·76 | ......... 69·46 |
| 2 | N | ......... | 28 | ......... | 8·14 | |
| 28 | H | ......... | 28 | ......... | 8·14 | ......... 8·02 |
| 6 | O | ......... | 48 | ......... | 13·96 | |
| $C^{40}N^2H^{26}O,2HO$ | | .... | 344 | ......... | 100·00 | |

The salts of hydrocinchonine are very soluble. — The *platinum-salt* dried at 100° contains 27·1 p. c. of platinum, corresponding to the formula $C^{40}N^2H^{26}O^4,2HCl,2PtCl^2$ (calc. 27·06 p. c. Pt.).

Hydrocinchonine dissolves easily in cold *alcohol* and *ether*.

# Oxycinchonine.

$$C^{40}N^2H^{24}O^4 = C^{40}N^2H^{22}O^4,H^2.$$
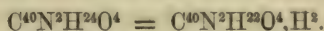
H. STRECKER. *Ann. Pharm*, 123, 379; abstr. *N. Br. Arch.* 115, 169.

An alcoholic solution of bibromocinchonine is boiled with alcoholic potash (or oxide of silver) so long as bromide of potassium continues to be formed; the free potash is neutralised by carbonic acid; the solution is evaporated; and the residue is treated with water to remove salts soluble in that liquid. The insoluble portion, dissolved in alcohol, yields crystals of oxycinchonine on cooling and evaporating the solution.

| | | | *Colourless crystalline laminæ.* | | | H. Strecker. mean. |
|---|---|---|---|---|---|---|
| 40 | C | ......... | 240 | ......... | 74·07 | ......... 73·80 |
| 2 | N | ......... | 28 | ......... | 8·64 | |
| 24 | H | ......... | 24 | ......... | 7·41 | ......... 7·45 |
| 4 | O | ......... | 32 | ......... | 9·88 | |
| $C^{40}N^2H^{24}O^4$ | | .... | 324 | ......... | 100·00 | |

Isomeric with quinine, quinidine, and quinicine, also with Schützenberger's product obtained by the action of nitrous acid on cinchonine (p. 202).

Oxycinchonine does not produce the green colour which is produced by quinine with *chlorine-water* and ammonia.

It dissolves in acids, forming solutions which are not fluorescent. The mono-acid salts crystallise with difficulty; the sulphate and oxalate most easily. Bi-acid salts have not been obtained.

*Sulphate of Oxycinchonine.* — Crystals which lose their water partially in dry air, and completely at 100°.

|  |  | *at* 100°. |  |  | H. Strecker. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ | ............ | 324 | ........ | 86·86 |  |
| HO | ............ | 9 | ........ | 2·41 |  |
| SO³ | ............ | 40 | ........ | 10·73 | ........ 10·8 |
| $C^{40}N^2H^{24}O^4,HO,SO^3$ | .... | 373 | ........ | 100·00 |  |

*Platinum-salt.* — Bichloride of platinum throws down from the solution in hydrochloric acid, pale yellow flocks, which are sparingly soluble in hot water, and insoluble in alcohol and ether. Contains 26·3 p. c. of platinum, corresponding to the formula $C^{40}N^2H^{24}O^4,2HCl,2PtCl^2$ (calc. 26·87 p. c. Pt.).

Oxycinchonine dissolves in *alcohol*, and slightly in *ether*.

## Cinchonine-sulphuric Acid.

$$C^{40}N^2H^{24}SO^5 = C^{40}N^2H^{24}O^2,SO^3.$$
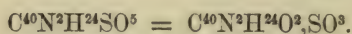
SCHÜTZENBERGER. *Compt. rend.* 47, 235; *J. pr. Chem.* 75, 254; *Ann. Pharm.* 108, 353; *Chem. Centr.* 1858, 684; *Kopp's Jahresber.* 1852, 370.

*Acide sulphocinchonique.*

Cinchonine is dissolved in fuming oil of vitriol; the solution, after standing for some time, is diluted with water and neutralised with baryta; the filtrate is evaporated; and from the baryta-salt which remains the cinchonine-sulphuric acid is separated by means of sulphuric acid.

Solid, amorphous, acid mass. — Dissolves in all proportions in water.

*Baryta-salt.* — Transparent, friable, vitreous mass, having a slightly bitter taste. — Non-deliquescent: soluble in all proportions in water. The salt, dried at 100°, contains 28·13 p. c. of sulphate of baryta, corresponding to the formula $C^{40}N^2H^{23}BaO^2,SO^3$ (by calc. 28·03 p. c. BaO,SO³).

The acid dissolves in *alcohol*.

## Methyl-cinchonine.

$$C^{42}N^2H^{26}O^2 = C^{40}N^2H^{21}(C^2H^3)O^2,H^2.$$
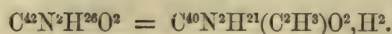
C. STAHLSCHMIDT. *Ann. Pharm.* 91, 218; *Pharm. Centr.* 1854, 680; *J. pr. Chem.* 63, 89; *Kopp's Jahresber.* 1854, 509.

Powdered cinchonine, digested with iodide of methyl, evolves heat and is converted into hydriodate of methyl-cinchonine, from an aqueous solution of which, oxide of silver throws down iodide of silver. — The methyl-cinchonine remaining in solution is obtained by evaporation as a brown crystalline mass, which deposits oily drops with water.

The salts of methyl-cinchonine crystallise with difficulty: they dissolve easily in water and alcohol. An aqueous solution of the base precipitates the salts of the sesquioxides.

*Hydriodate of Methyl-cinchonine.* — Deposited from its solution in boiling water in fine needles on cooling. It is not altered by iodide of methyl at 100°, nor decomposed, in aqueous solution, by ammonia, potash, or soda.

|  |  | *at* 100°. |  |  |  | Stahlschmidt. |
|---|---|---|---|---|---|---|
| 42 C | ............................. | 252 | ........ | 56·00 | ........ | 55·08 |
| 2 N | ............................. | 28 | ........ | 6·22 |  |  |
| 27 H | ............................. | 27 | ........ | 6·00 | ........ | 5·89 |
| 2 O | ............................. | 16 | ........ | 3·56 |  |  |
| I | ............................. | 127 | ........ | 28·22 | ........ | 29·19 |
| $C^{40}N^2H^{23}(C^2H^3)O^2,HI$ | .... | 450 | ........ | 100·00 |  |  |

*Chloride of mercury, chloride of gold,* and *bichloride of platinum* throw down double-salts from hydrochlorate of methyl-cinchonine. The platinum-salt contains, at 110°, 26·73 p. c. of platinum (calc. 26·81 p. c. Pt.).

# Methyl-cinchonidine.

$$C^{38}N^2H^{24}O^2 = C^{36}N^2H^{19}(C^2H^3)O^2,H^2 ?$$
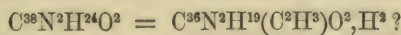
STAHLSCHMIDT. *Ann. Pharm.* 90, 221; *Pharm. Centr.* 1854, 680; *J. pr. Chem.* 63, 89; *Kopp's Jahresber.* 1854, 509.

*Methylchinidine.* See page 223.

Cinchonidine becomes warm when iodide of methyl is poured upon it, and is converted into hydriodate of methyl-cinchonidine, from an aqueous solution of which, oxide of silver precipitates iodide of silver, aqueous methyl-cinchonidine being formed at the same time. On evaporating the solution, the base remains as a brown crystalline mass.

*Hydriodate of Methyl-cinchonidine.* — Crystallises in white, shining needles on cooling the hot aqueous solution. Ammonia produces in the aqueous solution a milky turbidity, which disappears on the addition of more ammonia.

|  |  |  |  |  |  | Stahlschmidt. |
|---|---|---|---|---|---|---|
| 38 C | ............................. | 228 | ........ | 53·76 | ........ | 53·87 |
| 2 N | ............................. | 28 | ........ | 6·60 |  |  |
| 25 H | ............................. | 25 | ........ | 5·89 | ........ | 5·92 |
| 2 O | ............................. | 16 | ........ | 3·79 |  |  |
| I | ............................. | 127 | ........ | 29·96 | ........ | 29·84 |
| $C^{36}N^2H^{21}(C^2H^3)O^2,HI$ | .... | 424 | ........ | 100·00 |  |  |

## Acetyl-cinchonine.

$$C^{44}N^2H^{25}O^4 = C^{40}N^2H^{23}(C^4H^3O^2)O^2.$$
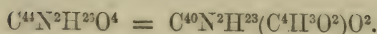
SCHÜTZENBERGER. *Compt. rend.* 47. 235.

By the action of chloride of acetyl, cinchonine is converted into hydrochlorate of acetyl-cinchonine, from which the base may be separated in the same way as benzoyl-cinchonine.

Semi-fluid resin, having a burning, not bitter taste. It saturates the same quantity of acid as would be saturated by the cinchonine contained in it.

## Benzoyl-cinchonine.

$$C^{54}N^2H^{28}O^4 = C^{40}N^2H^{23}(C^{14}H^5O^2)O^2.$$
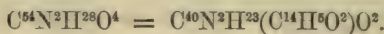
SCHÜTZENBERGER. *Compt. rend.*, 47, 233; *J. pr. Chem.* 75, 125; *Ann. Pharm.* 108, 351; *Chem. Centr.* 1858, 677; *Kopp's Jahresber.* 1858, 369.

Cinchonine dissolves in chloride of benzoyl, with evolution of heat, and after heating for some time, solidifies to a crystalline mass of hydrochlorate of benzoyl-cinchonine. The mass is digested with water, and the resulting solution obtained is decanted and precipitated with ammonia, whereby the benzoyl-cinchonine is thrown down as a soft resin, hardening as it cools.

White, amorphous, tasteless resin.

|  |  |  |  |  | Schützenberger. |
|---|---|---|---|---|---|
| 54 C | 324 | ........ | 78·64 | ........ | 78·47 |
| 2 N | 28 | ........ | 6·79 | | |
| 28 H | 28 | ........ | 6·79 | ........ | 6·98 |
| 4 O | 32 | ........ | 7·78 | | |
| $C^{40}N^2H^{23}(C^{14}H^5O^2)O^2$ | 412 | ........ | 100·00 | | |

Benzoyl-cinchonine heated on platinum-foil melts and *burns*, with partial volatilisation. When heated with *soda-lime*, it evolves benzene.

Insoluble in *water*. — Forms very soluble salts.

*Chloroplatinate of Benzoyl-cinchonine.*
at 140°.

|  |  |  |  |  | Schützenberger. |
|---|---|---|---|---|---|
| 54 C | 324 | ........ | 39·27 | ........ | 38·97 |
| 2 N | 28 | ........ | 3·39 | | |
| 30 H | 30 | ........ | 3·63 | ........ | 3·84 |
| 4 O | 32 | ........ | 3·89 | | |
| 6 Cl | 213 | ........ | 25·83 | | |
| 2 Pt | 197·4 | ........ | 23·99 | ........ | 23·94 |
| $C^{40}N^2H^{23}(C^{14}H^5O^2)O^2,2HCl,2PtCl^2$ | 824·4 | ........ | 100·00 | | |

Benzoyl-cinchonine dissolves in all proportions in *alcohol* and *ether*.

*Oxy-bromazo-nucleus* $C^{40}N^2BrH^{21}O^2$.

## Bromocinchonine.

$$C^{40}N^2BrH^{23}O^2 = C^{40}N^2BrH^{21}O^2,H^2.$$
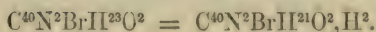
LAURENT. *Compt. rend.* 20, 1586; *N. Ann. Chim. Phys.* 24, 307; *Ann. Pharm.* 69, 9; *J. pr. Chem.* 46, 52.

*Bromcinchonin. Cinchonine bromée.* — According to Laurent = $C^{38}N^2BrH^{21}O^2$.

Bromine is poured upon moist bi-hydrochlorate of cinchonine, and after a few minutes the excess of bromine is washed off with alcohol. The mixture of salts then remaining is boiled with a little alcohol, which takes up hydrochlorate of cinchonine and hydrobromate of bromo-cinchonine, and leaves behind the corresponding nearly insoluble salts of sesqui-bromocinchonine. From the alcoholic solution the bromo-cinchonine is obtained by adding ammonia, boiling till the alcohol is driven off, and cooling. It is still to be purified by crystallisation.

|  |  | *Crystals.* |  |  |  | Laurent. |
|---|---|---|---|---|---|---|
| 40 C | ............ | 240 | ........ | 62·02 | ........ | 59·3 |
| 2 N | ............ | 28 | ........ | 7·23 |  |  |
| Br | ............ | 80 | ........ | 20·67 |  |  |
| 23 H | ............ | 23 | ........ | 5·94 | ........ | 5·6 |
| 2 O | ............ | 16 | ........ | 4·14 |  |  |
| $C^{40}N^2BrH^{23}O^2$ | .... | 387 | ........ | 100·00 |  |  |

*Hydrochlorate of Bromocinchonine.* — *Bi-acid.* Resembles the bi-acid hydrochlorate of cinchonine. Contains 15·4 p. c. chlorine (calc. 15·43 p. c. Cl).

*Platinum-salt.* Pale-yellow powder. Contains, after drying at 50°, 24·25 p. c. of platinum.

## Sesqui-bromocinchonine.

LAURENT. *Compt. rend.* 20, 1588; *N. Ann. Chim. Phys.* 24, 309.

Obtained, together with bromo-cinchonine, by the action of bromine on bihydrochlorate of cinchonine, and remains behind as a salt of hydrochloric or hydrobromic acid, insoluble in boiling alcohol. This insoluble residue is boiled with water; the solution is decomposed by ammonia, and the base thereby separated is crystallised from boiling alcohol.

Very slender, slightly bitter needles, having an alkaline reaction. — Melts when heated, and then suddenly blackens and froths up.

|  |  |  |  |  |  | Laurent. |
|---|---|---|---|---|---|---|
| 80 C | ............ | 480 | ........ | 56·27 | ........ | 55·45 |
| 4 N | ............ | 56 | ........ | 6·57 |  |  |
| 3 Br | ............ | 240 | ........ | 28·13 | ........ | 28·30 |
| 45 H | ............ | 45 | ........ | 5·28 | ........ | 5·18 |
| 4 O | ............ | 32 | ........ | 3·75 |  |  |
| $2C^{40}N^2H^{22·5}Br^{1·5}C^2$ | .... | 853 | ........ | 100·00 |  |  |

According to Laurent, it is not to be regarded as a mixture of bromo-cinchonine and bibromo-cinchonine, inasmuch as hot alcohol does not take up from it any of the former body, and its salts do not split up.

*Hydrochlorate.* — When hydrochloric acid is added to a solution of the base in boiling alcohol, rhombic tables of this salt crystallise on cooling. Right prismatic (Fig. 50), $u' : u = 107°$ to $108°$. Contains 14·5 p. c. of chlorine (calc. for the bi-acid salt, 14·2 p. c.).

When the residue insoluble in boiling alcohol, which is obtained in the preparation of sesqui-bromocinchonine, and consists of a mixture of hydrochlorate and hydrobromate, is digested with ammoniacal alcohol, it is at once dissolved ; and on adding hydrochloric acid to the solution, small rhombic tables, soluble in water, but very slightly soluble in boiling alcohol, make their appearance as the liquid cools. The crystals belong to the right prismatic system. (Fig. 50) $u' : u = 107°$ to 108°. They contain 43·60 p. c. C. and 4·47 H., with equal numbers of atoms of hydrochloric and hydrobromic acids, and are consequently *Bichlorobromhydrate de Cinchonine sesquibromée*, $C^{40}N^2Br^{1·5}H^{22·5}O^2,HCl,HBr$ (Laurent).

The *nitrate* forms shining needles, sparingly soluble in water and in alcohol. The *platinum-salt* is a pale-yellow precipitate, containing 23 p. c. platinum at $100°$ ; the salt contains by calculation 22·2 p. c. platinum ; but according to Laurent (*Compt. rend.* 20, 1588), the precipitate loses 2 at. of water, at 180°.

*Oxybromazo-nucleus*   $C^{40}N^2Br^2H^{20}O^2$.

## Bibromocinchonine.

$$C^{40}N^2Br^2H^{22}O^2 = C^{40}N^2Br^2H^{20}O^2,H^2.$$
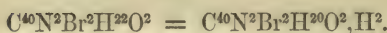
LAURENT.   *Compt. chim.* 1849, 312 ; *Ann. Pharm.* 72, 305.
H. STRECKER.   *Ann. Pharm.* 123, 379.

An excess of bromine, together with a little water, is poured upon hydrochlorate of cinchonine ; the mixture is warmed to complete the reaction, and to drive off the excess of bromine ; and the product is diluted with water, boiled, and filtered. Alcohol is then added ; and the whole is boiled afresh, and neutralised with ammonia : the bibromocinchonine then crystallises out on cooling (Laurent). Strecker removes the excess of bromine by means of a little alcohol, dissolves the residue in boiling alcohol, adds ammonia to the solution, and leaves it to crystallise.

Colourless, laminar needles, exerting a right-handed action on polarised light (Laurent).

| | | | | | | Laurent. | | Strecker. |
|---|---|---|---|---|---|---|---|---|
| 40 C | .............. | 240 | ........ | 51·50 | ........ | 51·20 | | |
| 2 Br | ................ | 160 | ........ | 34·34 | ........ | 34·00 | ........ | 33·2 |
| 2 N | ................ | 28 | ........ | 6·01 | | | | |
| 22 H | ................ | 22 | ........ | 4·72 | .......... | 4·40 | | |
| 2 O | ................ | 16 | ........ | 3·43 | | | | |
| $C^{40}N^2Br^2H^{22}O^2$ | .... | 466 | ........ | 100·00 | | | | |

Bibromocinchonine does not lose water at 160°; at 200° it blackens and puffs up, and forms a substance soluble in caustic potash and precipitable from the solution in brown flocks by acids (Laurent). — When it is boiled with alcoholic *potash*, or with alcohol and *oxide of silver*, bromide of potassium or bromide of silver is deposited, and oxycinchonine formed (Strecker).

*Combinations.* *With Water.* The (alcoholic?) solution of bibromocinchonine set aside for some days in an open vessel, deposits square based octahedral crystals of the size of pins' heads. The crystals lose 4·2 p. c. of water at 160° (2 at. = 3·72 p. c. HO) (Laurent).

Bibromocinchonine is insoluble in water.

*Hydrochlorate of Bibromocinchonine.* — $C^{40}N^2Br^2H^{22}O^2,2HCl$. Deposited from a boiling solution on cooling in rhombic tables, truncated on the four acute summits. — Isomorphous with hydrochlorate of sesquibromocinchonine. $u : u' = 104$ to $105°$; $p : i = 137°$ (Laurent).

Bibromocinchonine dissolves slightly in boiling *alcohol*.

*Oxychlorazo-nucleus* $C^{40}N^2Cl^2H^{20}O^2$.

# Bichlorocinchonine.

$$C^{40}N^2Cl^2H^{22}O^2 = C^{40}N^2Cl^2H^{20}O^2,H^2 ?.$$
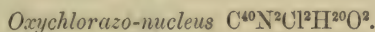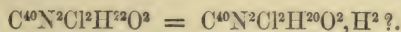
A. LAURENT *Compt. rend.* 20, 1588; *N. Ann. Chim. Phys.* 24, 304; *J. pr. Chem.* 46, 52; *Ann. Pharm.* 69, 9; *Kopp's Jahresber.* 1847 and 1848, 618.

*Chloré-cinchonine.* *Cinchonine bichlorée.*

When chlorine is made to act upon a warm concentrated aqueous solution of hydrochlorate of cinchonine, hydrochlorate of bichlorocinchonine is thrown down as a heavy crystalline powder, which is purified by crystallisation from boiling water. From a boiling aqueous solution of the salt, ammonia throws down the bichlorocinchonine in light flocks, crystallisable from boiling alcohol.

Microscopic needles, having an alkaline reaction, and containing 18·9 p. c. chlorine (calc. for $C^{40}N^2H^{22}Cl^2O^2 = 18·83$ p. c. Cl). Exerts a right-handed action on polarised light.

Bichlorocinchonine distilled with caustic potash yields chinoline. — It forms with acids, crystallisable salts resembling those of bromocinchonine and isomorphous therewith.

*Hydrobromate of Bichlorocinchonine.* — Shining needles, isomorphous with bihydrochlorate of cinchonine and hydrochlorate of bichlorocinchonine. The crystals belong to the right prismatic system (Fig. 50), and exhibit the same faces as the cinchonine-salt, but from the predominance of the faces $i$ and $p$ they have the appearance of six-sided prisms bevelled by $u$ and $u'$. Angle $u : u' = 104°$; $p : i = 137°$. Contains 30·2 p. c. bromine, and may therefore be represented by the formula $C^{40}N^2Cl^2H^{22}O^2,2HBr$ (calc. 29·79 p. c. Br). Dissolves with difficulty in water.

*Hydrochlorate of Bichlorocinchonine.* — Crystals of the right prismatic system (Fig. 50) $u' : u = 106°$; $p : i = 136·5°$ to $137·5°$. — Dissolves slightly in water and in about 50 parts of alcohol.

|  |  | | | | | Laurent. |
|---|---|---|---|---|---|---|
| 40 C | ............................. | 240 | ........ | 53·33 | ........ | 51·81 |
| 2 N | ........................... | 28 | ........ | 6·22 | | |
| 24 H | ......................... | 24 | ........ | 5·33 | ........ | 5·18 |
| 2 Cl | ........................... | 71 | ........ | 15·78 | | |
| 2 Cl | ........................... | 71 | ........ | 15·77 | ........ | 16·40 |
| 2 O | ........................... | 16 | ........ | 3·57 | | |
| $C^{40}N^2Cl^2H^{22}O^2,2HCl$.... | | 450 | ........ | 100·00 | | |

*Nitrate of Bichlorocinchonine.* — Right prismatic. Small tetrahedrons of scalene triangles having two opposite edges truncated. Slightly soluble in water.

*Platinum-salt.* — Pale-yellow powder, losing 2·4 p. c. of water at 180° after drying at 100°.

|  |  | *at 100°.* | | | | Laurent. |
|---|---|---|---|---|---|---|
| $C^{40}N^2Cl^2H^{22}O^2$ | ...................................... | 377 | ........ | 46·71 | | |
| $H^2Cl^6$ | ...................................... | 215 | ........ | 26·64 | | |
| 2 Pt | ...................................... | 197 | ........ | 24·41 | ........ | 25·00 |
| 2 HO | ...................................... | 18 | ........ | 2·24 | ........ | 2·40 |
| $C^{40}N^2H^{22}Cl^2O^2,2HCl,2PtCl^2 + 2aq.$ | .... | 807 | ........ | 100·00 | | |

## Primary Nucleus $C^{40}H^{26}$.

## Blue Galbanum-oil.

$$C^{40}H^{30}O^2 = C^{40}H^{28},H^2O^2.$$
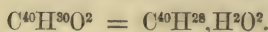
Mössmer (& Hlasiwetz). *Wien. Acad. Ber.* 43, 477; *Ann. Pharm.* 119, 257; *J. pr. Chem.* 86, 159. *Zeitschr. Ch. Pharm.* 4, 512; *Chem. Centr.* 1861, 673; *Repert. Chim. pure*, 3, 462; *Kopp's Jahresber.* 1861, 687.

Purified galbanum-resin submitted to dry distillation, yields water, a greenish-yellow oil, and crystals of umbelliferone. The oil is freed from the crystalline body by repeated boiling with water, and at last with very dilute potash; it is then dehydrated by heating it to 110° in a current of air, and rectified, the first and last portions of the distillate being rejected.

Pure blue, thick oil, of the colour of ammoniacal oxide of copper. Boils at 289°. Does not solidify in the cold. Has a slightly aromatic odour, and an acrid, very bitter taste.

|  |  | | | | | Mössmer. mean. |
|---|---|---|---|---|---|---|
| 40 C | ............. | 240 | ........ | 83·91 | ........ | 83·75 |
| 30 H | ............. | 30 | ........ | 10·49 | ........ | 10·44 |
| 2 O | ............. | 16 | ........ | 5·60 | ........ | 5·81 |
| $C^{40}H^{30}O^2$ | ........ | 286 | ........ | 100·00 | ........ | 100·00 |

*Bromine* converts the oil into a resin, with evolution of hydrobromic

acid. — *Nitric acid* colours it a yellowish-red, turning darker on heating.
— *Oil of vitriol* colours it brown-yellow. — Galbanum oil is decolorised
by warming with anhydrous *phosphoric acid*, and when distilled there-
with, yields a yellowish oil, boiling at 250° to 253°, and containing, on
the average, 86·81 p. c. C., 10·76 H., and 2·43 O., corresponding to the
formula $C^{80}H^{58}O^2$ (calc. 86·66 p. c. C., 10·47 H.). The yellow oil there-
fore stands in the same relation to the blue oil as ether to alcohol. — The blue
oil boiled with *sodium* in a retort the beak of which inclines upwards,
till the colour of the distillate disappears, yields a colourless oil, having
an odour of herbs and a mild taste, and boiling at 254° : it contains 88·74
p. c. C. and 11·24 H., corresponding to the formula $C^{40}H^{30}$ (calc.
88·88 p. c. C., 11·12 H). — The blue oil is not altered by *alkalis*, or by
distillation with *lime*. — It is coloured light green by alcoholic *sesqui-
chloride of iron*.

The oil dissolves in *alcohol* with deep blue colour.


## Galbanum-resin.

MEISSNER.  *N. Tr.* 1, 1, 3.
JOHNSTON.  *Phil. Trans.* 1840, 362.
MÖSSMER.  *Wien. Acad. Ber.* 43, 477 ; *Ann. Pharm.* 119, 257.
HLASIWETZ & BARTH.  *Wien. Acad. Ber.* 49, 203 ; *Chem. Centr.* 1864,
    806.


Galbanum is freed from volatile oil by distillation with water ; the
remaining resin is separated from the supernatant milky liquid, and
boiled with milk of lime ; and the dark-yellow filtrate is precipitated
by hydrochloric acid, which throws down whitish-yellow flocks to
be purified by washing, dissolving in ether, and evaporating (Möss-
mer). Meissner and Johnston investigated the alcoholic extract
purified by boiling with water.

Galbanum-resin forms whitish-yellow flocks, which soften and melt
when warmed. On evaporating its ethereal solution, it remains as a
honey-yellow mass, no longer completely soluble in alcohol (Mössmer).
Tasteless (Meissner).

| | | *Calculation according to* Hlasiwetz. | | | | Johnston. *a.* | | *b.* | | Mössmer. *melted.* | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 52 C | ........ | 312 | .... | 72·56 | .... | 73·16 | .... | 73·20 | .... | 71·60 | .... | 72·05 |
| 38 H | ........ | 38 | .... | 8·84 | .... | 8·47 | .... | 8·12 | .... | 8·44 | .... | 8·00 |
| 10 O | ........ | 80 | .... | 18·60 | .... | 18·37 | .... | 18·68 | .... | 19·96 | .... | 19·95 |
| $C^{52}H^{38}O^{10}$. | | 430 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 |

*a* was heated to 66 or 92° ; *b* to 150° for 2 hours, whereby 10 per cent. was
volatilised (Johnston).

Galbanum-resin submitted to dry distillation yields a blue oil
(p. 238), water, and umbelliferone (Mössmer). Probably thus :

$$C^{52}H^{38}O^{10} = C^{40}H^{30}O^2 + C^{12}H^4O^4 + 4HO \text{ (Hlasiwetz).}$$
Umbelliferone.
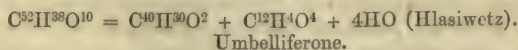
With warm *nitric acid*, it forms acetic and oxalic acids. — Dissolves in
oil of vitriol with dark yellowish-brown colour, without evolving sul-
phurous acid (Meissner). — A concentrated alcoholic solution, satu-

rated with hydrochloric acid gas and heated to 100°, yields umbelliferone and a brown mass, but no sugar (Mössmer). When melted with *caustic potash*, it froths up and evolves aromatic vapours, the residue containing resorcin (*infra*), oxalic acid, and one or more volatile fatty acids (Hlasiwetz & Barth).

Galbanum-resin dissolves slightly both in cold and in hot solutions of *caustic potash*, and forms with the latter a soap which floats on the surface of liquid, and is perfectly soluble in water (Meissner). — It dissolves partially in *bisulphide of carbon*, and easily in *alcohol*; and is completely soluble in commercial, but only partially soluble in absolute *ether* (Mössmer). It is not perceptibly soluble in alcohol of 50 p. c., and but very slightly soluble in hot *oil of turpentine* and *oil of almonds* (Meissner).

*Galbanum. Mother-resin.* — From *Galbanum officinale.* Brown and white; brittle in the cold, but becomes tough on warming. Has an unpleasant odour, and an acrid, bitter taste. An alcoholic solution reddens litmus. — Contains volatile oil, resin, and gum, together with woody fibre and other vegetable residue. — By dry distillation, it yields umbelliferone (Sommer, *N. Br. Arch.* 98, 1), a yellow water containing acetic acid, a pale-green, afterwards blue, and at last brownred oil, beside carbonic acid and hydrocarbons (Meissner), With nitric acid of sp. gr. of 1·2, it yields styphnic or other acids (Bottger & Will). It is more violently attacked than gum ammoniacum by nitric acid of sp. gr. 1·34, dissolving rapidly and forming camphretic acid (Schwanert, *Ann. Pharm.* 128, 123). — Forms a milky liquid with water and yields a volatile oil by distillation (Pelletier, *Bull. Pharm.* 4, 97).

*Volatile oil of galbanum* is colourless, of sp. gr. 0·8842 at 9° (Mössmer), 0·895 (Finkh, *N. Jahrb. Pharm.* 4, 285), 0·912 (Meissner). It exerts a right-handed action on polarised light, boils at 160°, and is isomeric with oil of turpentine. Hydrochloric acid gas passed into it, turns it red and forms crystals; dilute nitric acid renders it dark coloured without forming crystals in three months (Mössmer).

*Addendum* to vol. xi, p. 379.

## Resorcin.

$$C^{12}H^6O^4 \;=\; C^{12}H^6O^2,O^2?$$
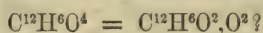
HLASIWETZ & BARTH. *Wien. Akad. Ber.* 49, 203; *Ann. Pharm.* 130, 354; *Chem. Centr.* 1864, 806. — *Zeitschr. Ch. Pharm.* 7, 285.

*Formation.* By melting guaiacum, galbanum, or ammoniacum resin with caustic potash.

*Preparation.* The portion of galbanum-resin soluble in alcohol is melted with 2 to 3½ parts of caustic potash, till the mass becomes homogeneous, the reaction being attended with much frothing and the evolution of aromatic vapours. The fused mass is at once poured into water and acidulated with sulphuric acid; and after cooling and filtering, the liquid is repeatedly shaken with ether, which takes up resorcin. The ethereal solution is evaporated, and the residue sub-

mitted to distillation, when a distillate is obtained consisting at first of a thick oil, and afterwards of resorcin, which solidifies to a crystalline mass. The product is purified either by rectifying and collecting the portion passing over between 269° and 279°, or by dissolving in a little warm water, adding baryta-water to alkaline reaction, and taking up the resorcin by ether, in which case the fatty acids are left in combination with baryta.

*Properties.* Colourless, rhombic tables, or short thick prisms, melting and volatilising slightly at 99°, and boiling without decomposition at 271°. Neutral; inodorous. Has a disagreeable, harsh, sweet taste. Vapour-density = 4·1, which is a little too high, owing to decomposition indicated by a deep-brown coloration of the substance.

|  |  |  |  |  | Hlasiwetz & Barth. |
|  |  |  |  |  | *mean.* |
| 12 C | 72 | | 65·45 | | 65·3 |
| 6 H | 6 | | 5·45 | | 5·7 |
| 4 O | 32 | | 29·10 | | 29·0 |
| $C^{12}H^6O^4$ | 110 | | 100·00 | | 100·0 |

|  | Volume. | Vapour-density. |
|---|---|---|
| Carbon-vapour | 12 | 4·9920 |
| Hydrogen | 6 | 0·4158 |
| Oxygen | 2 | 2·2186 |
| Resorcin-vapour | 2 | 7·6264 |
|  | 1 | 3·8132 |

Isomeric with hydrokinone (xi, 161) and pyrocatechin (xi, 379); homologous with orcin (xii, 353).

Resorcin *burns* with a luminous flame. — When exposed to the air it acquires a faint reddish colour. — Saturated *bromine-water* throws down from moderately dilute aqueous resorcin soft needles of tribromo-resorcin, $C^{12}Br^3H^3O^4$, which dissolve with difficulty in cold, and easily in boiling water and in alcohol, and give off water of crystallisation at 100°. — Aqueous resorcin, mixed with ammonia and exposed to the air, assumes a rose-red to brown colour, and leaves on evaporation a dark-blue residue, which dissolves in water and is reddened by acids. — *Chloride of lime* colours it a transient violet; *sesquichloride of iron* dark-violet to black, the colour disappearing on addition of ammonia, whilst sesquioxide of iron is precipitated. — Resorcin throws down suboxide of copper from *alkaline solutions of the oxide*, and reduces *nitrate of silver*.

Resorcin dissolves very easily in *water, alcohol,* and *ether,* also in *bisulphide of carbon* and *chloroform.*

*Oxygen-nucleus* $C^{40}H^{26}O^2$.

## Guaiaretic Acid.

$$C^{40}H^{26}O^8 = C^{40}H^{26}O^2,O^6.$$
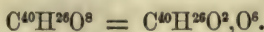
HLASIWETZ. *Ann. Pharm.* 112, 182; *Chem. Centr.* 1860, 97; *Kopp's Jahresb.* 1859, 514.

HLASIWETZ & v. GILM.  *Wien. Acad. Ber.* 43, 463; *Ann. Pharm.* **119,** 266; *J. pr. Chem.* 86, 363; *Zeitschr. Ch. Pharm.* 4, 499; *Chem. Centr.* 1861, 641; *N. J. Pharm.* 41, 88; *Kopp's Jahresb.* 1861, 685.

HLASIWETZ & BARTH.  *Wien. Acad. Ber.* 49, 1; *Ann. Pharm.* 130, 346; *N. Repert. Pharm.* 13, 193.

HADELICH.  *Ueber die Bestandth. des Guajakharzes.*  Dissert. Gött. 1862; *J. pr. Chem.* 87, 321; *Zeitschr. Ch. Pharm.* 6, 104; *Chem. Centr.* 1863, 305; *Rép. Chim. pure* 5, 271; *Kopp's Jahresb.* 1862, 466.

*Source.*  In guaiac-resin.  (See below.)

*Preparation.*  One pound of guaiac-resin is dissolved in a sufficient quantity of alcohol to form a thin syrup; the solution, clarified by straining, is mixed with a strong warm alcoholic solution of half a pound of caustic potash; and the mixture is left to itself for twenty-four hours.  It then solidifies to a pulpy mass, which is to be purified by pressing it between linen cloth, mixing it repeatedly with strong alcohol and pressing, and lastly by triturating and washing it with cold water, then dissolving in a large quantity of boiling weak alcohol.  On cooling the filtrate it is obtained in crystals, which must be twice recrystallised.  The potash-salt of guaiaretic acid thus obtained is decomposed by hydrochloric acid, whereupon the guaiaretic acid is thrown down as a soft, sticky precipitate, which is washed and dissolved in alcohol, and crystallises from the solution by spontaneous evaporation (Hlasiwetz). — 2. The powdered resin is boiled for half an hour with half its weight of lime previously made into a milk; the liquid is strained off; and the solid residue is dried and exhausted with hot alcohol in a percolator.  The light-yellow tincture thus obtained is freed from alcohol by distillation; the residue is dissolved in solution of caustic soda of sp. gr. 1·3; and the soda-salt formed on cooling is pressed, recrystallised from water containing soda, and decomposed by hydrochloric acid (Hlasiwetz & v. Gilm).

*Purification.* — 1. By recrystallisation from alcohol. — 2. By recrystallisation from warm concentrated acetic acid.  The crystals are washed with strong acetic acid, with weaker acetic acid, and with water, in succession. — 3. The alcoholic solution of the acid, diluted with water till it becomes turbid, deposits crystals on standing over night, as is also the case with an alcoholic solution of the soda or potash-salt diluted with a large quantity of water, after addition of hydrochloric acid (Hlasiwetz & v. Gilm).  The pure acid remains colourless in the air; its alcoholic solution assumes a pure grass-green colour with sesquichloride of iron, but is not rendered blue or green by chlorine-water; neither does the solution, diluted with water to a milk, turn blue on dropping red fuming nitric acid into it (Hlasiwetz & v. Gilm).

*Properties.*  The crystals, which are hydrated, according to Hadelich, are obtained in the anhydrous state by melting or by long exposure to heat. — They exert a left-handed action on polarised light, $[\alpha]j = 13·25°$ (Hadelich).  When rapidly distilled, the greater part volatilises unchanged (Hlasiwetz & v. Gilm).

|  | Dried. |  |  |  | Hlasiwetz & v. Gilm. mean. |  | Hadelich. mean. |
|---|---|---|---|---|---|---|---|
| 40 C | 240 | ........ | 72·72 | ........ | 72·53 | ........ | 71·93 |
| 26 H | 26 | ........ | 7·87 | ........ | 7·91 | ........ | 7·85 |
| 8 O | 64 | ........ | 19·41 | ........ | 19·56 | ........ | 20·22 |
| $C^{40}H^{26}O^8$ | 330 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

*Decompositions.* 1. Guaiaretic acid, submitted to *dry distillaton*, yields a thick yellow oil, consisting of guaiacol, guaiacin, and pyroguaiacin, the last of which speedily crystallises out (Hlasiwetz & v. Gilm). — 2. *Burns* on platinum-foil with luminous flame, leaving no residue. — 3. *Nitric acid* acts violently upon it, forming a yellow, brittle resin (Hlasiwetz & v. Gilm), but no oxalic acid (Hadelich). — 4. Guaiaretic acid dissolves in oil of vitriol with purple colour; water added to the solution throws down a white product. — 5. *Bromine* converts its solution in bisulphide of carbon into bromoguaiaretic acid. *Chlorine* evolves a large quantity of hydrochloric acid, and forms a red, glutinous, non-crystallisable resin. *Pentachloride of phosphorus* acts in a similar manner (Hlasiwetz & v. Gilm). Hydrochloric acid passed into the alcoholic solution does not form an ether (Hadelich). — 6. The acid melted with caustic *potash* yields the same products as guaiac-resin, with the exception of the acid, which turns alkalis green (Hlasiwetz & Barth). — 7. *Chloride of acetyl* forms a substitution-product, which crystallises from alcohol in granules (Hlasiwetz).

*Combinations.* — *With Water.* *Mono-hydrated Guiaiaretic acid.* Crystallises from alcohol in soft small nodules and scales, having a faint odour of vanilla; from acetic acid in inodorous brittle needles; from alcohol diluted with water in shining, thin laminæ (Hlasiwetz & v. Gilm). Rhombic pyramids having their terminal summits acuminated (Hadelich). Melts at 75° to 80°, and if cooled immediately solidifies to a crystalline mass; but if heated above its melting-point, it solidifies to a resin (Hlasiwetz & v. Gilm). Loses 6·73 p. c. of water on melting (Hadelich) (1 at. = 5·17 p. c.).

The acid is perfectly insoluble in water. It forms with bases *mono-* and *semi-acid salts,* and is therefore bibasic (Hlasiwetz & v. Gilm); but according to Hadelich, who obtained a quadrimetallic lead-salt, it is quadribasic. — The salts of the alkalis are crystallisable, those of the earths and metallic oxides are amorphous precipitates. The semi-acid (neutral) salts of the alkalis are obtained only with excess of alkali. Their solutions, after boiling, deposit mono-acid salts on cooling, while the solutions of the mono-acid salts suffer further change, a mixture of free acid and acid salt being deposited. The salts are decomposed by mineral acids (Hlasiwetz & v. Gilm).

Guaiaretic acid dissolves very slightly in cold or warm *ammonia-water.* Sal-ammoniac precipitates the acid from the potash-salt (Hlasiwetz & v. Gilm).

*Potash-salt.* — A. *Bibasic.* — A hot moderately strong solution of caustic potash dissolves guaiaretic acid, and on cooling deposits fine scales of the salt. Strong solution of potash solidifies, on addition of the acid, to a pulpy mass, a solution of which in warm alcohol deposits the salt in scales and laminæ on cooling. — The salt is also thrown

down by alcoholic potash from an alcoholic solution of the acid in the form of an indistinctly crystalline precipitate. — Contains, at 100°, sometimes 4 at., sometimes 6 at. water, which are expelled at 140°. By dry distillation it yields white vapours, water, and a little empyreumatic oil. — A solution of the salt in dilute alcohol, after boiling for some time and cooling, deposits the mono-acid salt (Hlasiwetz & v. Gilm).

| | | a. | | Hlasiwetz & v. Gilm. mean. |
|---|---|---|---|---|
| 40 C | 240 | ........ | 54·30 | ........ | 54·57 |
| 28 H | 28 | ........ | 6·33 | ........ | 6·44 |
| 2 K | 78 | ........ | 17·66 | ........ | 17·28 |
| 12 O | 96 | ........ | 21·71 | ........ | 21·71 |
| $C^{40}H^{24}K^2O^8 + 4HO$ | 442 | ........ | 100·00 | ........ | 100·00 |

| | | b. | | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|
| 40 C | 240 | ........ | 52·17 | ........ | 52·33 |
| 30 H | 30 | ........ | 6·52 | ........ | 6·26 |
| 2 K | 78 | ........ | 16·99 | ........ | 16·58 |
| 14 O | 112 | ........ | 24·32 | ........ | 24·83 |
| $C^{40}H^{24}K^2O^8 + 6HO$ | 460 | ........ | 100·00 | ........ | 100·00 |

*a* lost 8·16 p. c. of water at 140° (4 at. = 8·16 p. c.) ; *b* was likewise dried at 100° before analysis. Both salts exhibited, at 140°, the composition of the semi-acid salt, *a* containing 23·0, *b* 22·3 p.c. KO (by calc. 23·15).

B. *Mono-acid.* — Friable crystals, obtained also by adding carbonate of potash to a solution of the acid in weak alcohol, heating, and adding dilute alcohol till solution is effected. Decomposed by prolonged boiling of the solution. — Gives off 4·8 p. c. of water at 120° (2 at. = 4·66 p. c. HO) (Hlasiwetz & v. Gilm).

| | | at 100°. | | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|
| 40 C | 240 | ........ | 62·17 | ........ | 61·42 |
| 27 H | 27 | ........ | 6·99 | ........ | 7·20 |
| K | 39 | ........ | 10·10 | ........ | 9·83 |
| 10 O | 80 | ........ | 20·74 | ........ | 21·55 |
| $C^{40}H^{25}KO^8 + 2HO$ | 386 | ........ | 100·00 | ........ | 100·00 |

*Soda-salt.* — A. *Bibasic.* — Alcoholic soda throws down from an alcoholic solution of the acid, an abundant precipitate, which when dissolved by heating it with caustic soda and water, quickly crystallises in shining laminæ. — Dissolves in a hot mixture of water with an equal quantity of alcohol, the solution depositing the mono-acid salt on cooling (Hlasiwetz & v. Gilm).

| | | at 100°. | | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|
| 40 C | 240 | ........ | 58·29 | ........ | 58·05 |
| 28 H | 28 | ........ | 6·83 | ........ | 6·84 |
| 2 Na | 46 | ........ | 11·22 | ........ | 11·47 |
| 12 O | 96 | ........ | 23·66 | ........ | 23·64 |
| $C^{40}H^{24}Na^2O^8 + 4HO$ | 410 | ........ | 100·00 | ........ | 100·00 |

The salt dried at 120° contains 12·35 p. c. of sodium, and is therefore anhydrous (calc. 12·30 p. c. Na).

B. *Mono-acid.* — Small shining laminæ, which, after drying at

100°, lose 7·01 p. c. of water at 120° (2 at. HO = 4·86 p. c.) (Hlasiwetz and v. Gilm).

| | | at 100°. | | | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|---|
| 40 C | .................................. | 240 | ........ | 64·86 | ........ 65·01 |
| 27 H | .................................. | 27 | ........ | 7·29 | ........ 7·58 |
| Na | ..... ....................... | 23 | ........ | 6·21 | ........ 6·14 |
| 10 O | ............. .................... | 80 | ........ | 21·64 | ........ 21·27 |

$C^{40}H^{25}NaO^8 + 2HO$ .... 370 ........ 100·00 ........ 100·00

| | at 120°. | | | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|
| 40 C | ............ .... 240 | ........ | 68·18 | ........ 67·91 |
| 25 H | ................. 25 | ........ | 7·10 | ........ 7·62 |
| Na | ............. 23 | ........ | 6·53 | ........ 6·39 |
| 8 O | ................ 64 | ........ | 18·19 | ........ 18·08 |

$C^{40}H^{25}NaO^8$ .... 352 ........ 100·00 ........ 100·00

*Baryta-salt.* — The bibarytic salt, precipitated from chloride of barium by the potash-salt, is amorphous and chalk-white.

| | | | | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|
| $C^{40}H^{24}O^6$ | ........ 312 | ........ | 67·09 | |
| 2 BaO | ............. 153 | ........ | 32·91 | ........ 32·61 |

$C^{40}H^{24}Ba^2O^8$ .... 465 ........ 100·00

*Lead-salt.* — *Quadribasic ?* — An alcoholic solution of the acid is added to boiling alcoholic basic acetate of lead, in quantity not sufficient to produce complete precipitation; the whole is warmed for an hour without access of air; and the precipitate is washed by decantation with boiling alcohol and water. — White precipitate, which, after drying at 100°, does not give off any water at 130° (Hadelich).

| | at 130°. | | | Hadelich. mean. |
|---|---|---|---|---|
| $C^{40}H^{22}O^9$ | ........ 326 | ........ | 43·94 | |
| 4 Pb | ................ 416 | ........ | 56·06 | ....... 55·79 |

$C^{40}H^{22}Pb^4O^8$ .... 742 ........ 100·00

Guaiaretic acid dissolves in 1·86 parts of *alcohol* of 90·2 p. c. at 15°, and in the same quantity of *ether.* It is soluble in *bisulphide of carbon, chloroform, acetic acid, acetate of ethyl,* and *benzene* (Hadelich).

*Oxy-bromine-nucleus* $C^{40}Br^4H^{22}O^2$.

# Bromoguaiaretic Acid.

$$C^{40}Br^4H^{23}O^8 = C^{40}Br^4H^{22}O^2, O^6.$$
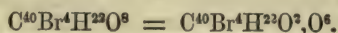
HLASIWETZ & v. GILM. *Ann. Pharm.* 119, 275.

Bromine is dropped into a solution of guaiaretic acid in bisulphide of carbon till the liquid passes through carmine-red and violet, and assumes a brown colour: the solution is then evaporated over the water-bath. The crystals which remain are washed with cold

alcohol and dissolved in a large quantity of boiling alcohol, from which the acid is rapidly deposited on cooling.

Colourless, loose, shining short needles.

| | | at 100°. | | | Hlasiwetz & v. Gilm. mean. |
|---|---|---|---|---|---|
| 40 C | ..................... | 240 | ........ | 37·15 | ........ 37·37 |
| 4 Br | ................ | 320 | ........ | 49·39 | ........ 49·35 |
| 22 H | ................ | 22 | ........ | 3·40 | ........ 3·76 |
| 8 O | ................ | 64 | ........ | 10·06 | ........ 9·52 |
| $C^{40}Br^4H^{22}O^8$ | .... | 646 | ........ | 100·00 | ........ 100·00 |

*Appendix to Guaiaretic Acid..*

## 1. Guaiac Beta-resin.

$$C^{40}H^{20}O^{12} \text{ or } C^{28}H^{14}O^6.$$
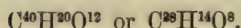
Obtained as a residue insoluble in ether in the preparation of guaiaconic acid (p. 155). This residue is completely freed from guaiaconic acid by mixing it with sand and treating with ether; it is then dissolved in alcohol, decolorised by animal charcoal, and precipitated by pouring the solution into ether. The brown flocks are still to be purified by again dissolving and precipitating, and lastly by precipitating the alcoholic solution with water.

Red-brown powder, melting at 200° to a black mass. Neutral. Dissolves in alkalis, from which it is precipitated by acids. The alcoholic solution is precipitated by basic acetate of lead, but not by the neutral acetate. — Dissolves easily in alcohol, acetic acid, and acetate of ethyl, but is insoluble in ether, chloroform, and benzene. Contains at 100°, on an average, 67·81 p. c. C., 5·81 H., and a little nitrogen (Hadelich).

## 2. Guaiac-yellow.

HADELICH. *Dissertation*, page 9.

*Yellow colouring matter* of Guaiac resin. Observed by Pelletier.

Powdered guaiac resin is boiled with milk of lime, and the liquid is filtered and evaporated, so that, by the action of carbonic acid, the greater part of the lime may be precipitated as carbonate, whilst most of the guaiaretic acid deposited. The residue is exhausted with water, and the solution is supersaturated with acetic acid, filtered, and left to stand for 14 days or longer, when small pale-brown tables crystallise out. The crystals dissolve with difficulty in a large quantity of water, leaving resin, but are easily soluble in ether and alcohol, and crystallise from the latter on evaporation.

Pale-yellow, quadratic octohedrons with truncated summits, or quadratic tables. Inodorous, bitter, and grating between the teeth. Contains nitrogen. Neutral. Without action on polarised light.

When heated in a tube, it yields a distillate of brown oil. — Melts

on platinum-foil to a greenish-yellow mass, with loss of water, and afterwards burns, evolving suffocating vapours. — Dissolves in *oil of vitriol*, forming a fine blue solution, which becomes green and yellow as it absorbs water, but turns blue again on warming. It is decolorised by the addition of water. — Dissolves in fuming nitric acid with orange colour, which is changed to red by oil of vitriol.

Difficultly soluble in *water*, and scarcely at all in boiling *hydrochloric acid*, either strong or dilute, by which it is not decomposed. — Dissolves easily in aqueous *ammonia, alkalis,* and *alkaline earths,* with deep yellow colour, which is destroyed by acids. — The aqueous solution is not precipitated by salts of the metals, with the exception of the *neutral* and *basic acetates of lead.*

Dissolves easily in *bisulphide of carbon, alcohol, ether,* and *acetate of ethyl,* and with difficulty in *chloroform, benzene,* and *oil of turpentine.*

## 3. Guaiac-resin.

BRANDE. *Ann. Chim.* 98, 140.
WOLLASTON. *Gilb.* 39, 294.
BUCHNER. *Repert.* 3, 281.
PAGENSTECHER. *N. Tr.* 3, 1, 447.
TADDEI. *N. Tr.* 4, 2, 159.
PLANCHE. *J. Pharm.* 6, 16; *N. Tr.* 4, 2, 261; *Berl. Jahrb.* 1820. 16.
BRANDES. *Berl. Jahrb.* 1821, 143.
UNVERDORBEN. *N. Tr.* 8, 1, 57. — *Pogg.* 8, 481; 16, 369.
TROMSDORFF. *N. Tr.* 21, 1, 27.
FR. JAHN. *N. Br. Arch.* 33, 269.
SCHACHT. *N. Br. Arch.* 35, 3.
W. MÜLLER. *N. Br. Arch.* 35, 262.
SCHÖNBEIN. *Pogg.* 67, 97; 73, 489; 75, 351.
OSANN. *Pogg.* 67, 372.

From *Guaiacum officinale* (*Handbuch,* viii [2], 20). Obtained partly by spontaneous exudation: *Gummi Guaiacum, Resina Guaiaci nativa;* partly by exhausting the wood with alcohol: *Resina Guaiaci.* — Greenish externally, reddish and greenish-brown within; easily triturable to a grey-white powder; translucent; of conchoïdal and splintery fracture. Sp. gr. 1·205 (Pfaff), 1·2289 (Brande). Becomes tough when chewed. The resin prepared from the wood melts in boiling water. In the form of powder and when heated it has a balsamic odour. Tastes sweetish-bitter, and hot and harsh in the throat: the resin of the wood, however, is tasteless (Buchner; Trommsdorff).

Guaiac resin contains 71·00 p. c. C., 7·03 H., and 21·97 O. It is, however, not a single substance, but contains $\frac{1}{16}$th its weight of a resin insoluble in ether, besides yellow-colouring matter (Pelletier, *J. Pharm.* 27, 386). The commercial resin contains, besides resin proper, bark, woody fibre, gum, and brown extractive (Buchner, *Repert.* 3, 281). On evaporating its solution in cold alcohol on flat plates, and heating the residue for 12 hours to 120°, there remains a transparent, ruby-red, brittle resin, containing 68·54 p. c. C., 6·83 H., and 24·63 O. (Johnston, *Phil. Trans.* 1839, 291).

Guaiac resin contains, in 100 parts, 10·50 parts of guaiaretic acid (p. 241) 70·35 of guaiaconic acid (p. 155), 9·76 of beta-resin, besides gum, woody fibre, solid constituents insoluble in water, guaiacic acid (xi, 397 ; and xvii, 252) and guaiac yellow (p. 240) (Hadelich).

According to Unverdorben, guaiac resin consists of a portion which is soluble in all proportions in aqueous ammonia, but insoluble in boiling carbonate of soda, and precipitates acetate of copper at the boiling heat ; together with a large quantity of a second resin, which forms with ammonia a tarry compound, difficultly soluble in water, and giving off its ammonia on boiling. — Jahn distinguishes three resins, two of which are soluble in ether, and separable from one another by ammonia.

According to Kosmann (*N. J. Pharm.* 38, 82) the purified resin is decomposed by heating with dilute sulphuric acid, with separation of guaiaretin and formation of sugar.    This observation was found by Hadelich not to be correct, either in the case of crude guaiac resin or of any of its constituents.    Kosmann (*Par. Soc. Bull.* 5, 391), however, still maintains the modified statement that guaiac resin yields with acids a very small quantity of a brown substance, which reduces cuprate of potash.

Pelletier's pure guaiac resin, or *guaiacin*, is obtained by precipi-tating the tincture with neutral acetate of lead, washing the precipi-tate with water and alcohol, decomposing it with hydrosulphuric acid, and extracting with alcohol.   Or alcoholic guaiac resin is treated with hydrated oxide of lead, whereby an easily decomposible compound is formed. — It possesses, in a high degree, the property of becoming blue in the air, or under water containing air, or under boiled water, with evolution of hydrogen, and is again decolorised by hydrosulphuric acid and other bodies (Pelletier, *J. Pharm.* 27, 386).

Alcoholic guaiac resin deposits, on standing, delicate white groups of needles, which redden litmus, melt, and volatise incompletely, with decomposition ;  Landerer's *guaiacin*.    The crystals assume a fine grass-green colour with nitrous acid or strong nitric acid, and a pale-green with chlorine-water or iodine, the colour disappearing on the volatilisation of the iodine.    They are insoluble in oil of vitriol and in water, but strong hydrochloric acid takes up a portion which is precipi-tated by alkalis.    They are insoluble in caustic potash or its carbonate, but soluble in boiling ammonia-water : they do not dissolve in cold alcohol or ether, but are soluble in the boiling liquids, from which they crystallise on cooling (Landerer, *Repert.* 52, 94).    Landerer also ob-tained from ammoniacal tincture of guaiacum, splendid green prisms containing ammonia, only partially soluble in water and alcohol (*Repert.* 56, 83).

Guaiacum wood contains a resin resembling commercial guaiac resin in its behaviour with solvents, together with guaiacic acid, guaiacin, Riegel's gum, and salts.    It gives up to boiling water guaiacic acid (xi, 397), precipitable by basic acetate of lead, and afterwards yields to alcohol, resin and guaiacin, which are deposited on evapo-rating the alcohol.    *Guaiacin* forms neutral yellow nodules, having a bitter and acrid taste, soluble in boiling water, and more easily in ether. It is not turned blue by nitric acid, as is the resin soluble in alcohol and ether (Riegel, *Jahrb. pr. Pharm.* 14, 243). — Guaicum bark contains an acrid extractive substance, and a dark-brown, brittle resin : the tincture of this last named body does not acquire a blue colour with

fuming nitric acid, and differs, therefore, from ordinary guaiac resin (Trommsdorff).

Guaiac resin *burns* with a powerful aromatic odour. — It melts easily, begins to decompose about 300°, and when subjected to *dry distillation* yields at first water smelling of the resin, then a slightly acid water, and a yellow, light oil of penetrating odour, and at last a thick, yellowish-brown, heavy oil, whilst charcoal remains behind (Unverdorben; Völckel; Sobrero). During the distillation carbonic acid and hydrocarbons are evolved (Brandes). No umbelliferone is obtained (Sommer).

When the product obtained by the dry distillation of guaiac resin in an iron retort is rectified, there pass over first guaiacene (x, 411) with a large quantity of water, then a heavier, thick product, and at last pyroguaiacin (xii, 349), which solidifies in a crystalline mass. On separating, by a second rectification, the middle portion from the first, which consists chiefly of guaiacene, and the last, which contains a large quantity of pyroguaiacin, there remains an oil which, when treated according to xii, 350, yields the pyroguaiacic acid (*Pyrojaksaüre*) of this work, *i.e.*, Völckel's guaiacol. According to Hlasiwetz, it is a mixture of two homologous oils of the formula $C^{14}H^8O^4$ and $C^{16}H^{10}O^4$, the latter of which may also be obtained from creosote (see xv, 161). See further below. Hlasiwetz's statement that the oil also contains furfurol was refuted by Schwanert (*Ann. Pharm.* 116, 285).

Powdered guaiac resin and tincture of guaiacum, as well as paper moistened with the tincture and dried, are turned blue by *ozonised oxygen*, but not by ordinary oxygen: they are coloured blue also by iodine, bromine, chlorine, the peroxides of manganese, lead, and silver, by oxide of silver, oxide of mercury, teroxide of gold, permanganic acid, chromic acid, hyponitric acid, alkaline hypochlorites, finely divided platinum, and by sesquichloride of iron, chloride of copper, and ferricyanide of potassium. The blue colour is destroyed by heat, and also by reducing agents, as phosphorus, finely divided tin, iron, zinc, and other metals, hydrosulphuric acid, hydroselenic acid, sulphurous acid, proto-salts of iron and tin, ferrocyanide of potassium, mineral acids, and alkalis. The colour disappears also spontaneously, the rate of its disappearance depending upon the nature of the substance producing it. After being frequently coloured and decolorised the tincture loses the property of turning blue (Schönbein).

Ordinary air also produces the blue coloration when a very small quantity of the tincture is placed in strong sunlight and shaken with a large quantity of air (Schönbein). The blue (or green) colour is not produced in carbonic acid, and in oxygen gas only on exposure to colourless or violet light, whilst the red rays of light concentrated to a focus, reduce the green to yellow again (Wollaston). See also Jodin (*N. J. Pharm.* (4) 1, 56; *Compt. rend.* 59, 857). The tincture, mixed with common salt, and submitted to the electric current, immediately becomes blue: crude impure salt, however, itself produces the blue coloration (Osann). See also Arnaudon (*Cimento* 8, 281; *Kopp's Jahresber.* 1858, 451); Regimbeau (*J. Pharm.* 15, 14); Schacht (*N. Br. Arch.* 35, 3); H. Schiff (*Ann. Pharm.* 111, 373).

Powdered guaiac-resin acquires a bright blue colour when triturated with gluten which is not spoiled, or with flour containing a large quantity of gluten, but in all cases exposure to air is necessary. The colour is not formed with starch (Taddei; Ridolfi). — Tincture of guaiacum

turns blue also, even without exposure to light, when dropped upon slices of the following fresh roots: *Cochlearia Armoracia* and *C. officinalis, Brassica Napus, Symphytum off., Borago off., Solanum tuberosum, Leontodon Taraxacum, Cichorium* (the sap of which also possesses the property), *Inula Helenium, Arcticum Lappa, Scorzonera hispanica, Glycyrrhiza glabra, Fumaria off., Eryngium campestre, Daucus Carota, Angelica Archangelica, Althœa off., Asparagus off., Saponaria off., Rumex acetosa, Iris germanica, Nymphœa alba, Colchicum autumnale* and *Allium Cepa.* Most of these roots lose the property on drying, and some even when heated to 100°. The fresh roots of *Rumex acutus, Fragaria Vesca, Polypodium Filix Mas,* and others do not produce the blue colour (Planche).

The substance producing the blue colour occurs in all parts of the potato, but the colour is most rapidly and vividly produced in the peel, and at the places where eyes occur. Boiled potatoes do not possess the colouring property (Schönbein, *Pogg.* 75, 357). See also Schacht, Van der Broek (*Scheikund. Onderzoek.* 5, 3; Stuck, 210; and 5, 6, Stuck, 226; abstr. *Pharm. Centr.* 1850, 635, and 645). Concerning the blue colour produced by *Vinum. Sem. Colchici,* see W. Müller (*N. Br. Arch.* 35, 362).

Gum arabic made with cold water colours powdered guaiacum blue, but this property is not possessed by a solution in hot water, nor by gum tragacanth. Milk behaves in a similar manner, fresh milk producing the blue colour, whilst the boiled liquid no longer possesses the property, even after cooling and saturating it with air (Planche).

Tincture of guaiacum is not coloured blue by peroxide of hydrogen, but on adding to the mixture a little platinum-black, it immediately assumes a deep blue colour; mercury also, and gold, silver, osmium, gluten, diastase, emulsin, myrosin, yeast, and all vegetable and animal substances which have the property of decomposing peroxide of hydrogen (ii, 77) act in the same way as platinum (Schönbein, *N. Repert.* 13, 338).

*Chlorine gas* and aqueous chlorine quickly colour powdered guaiacresin green, blue, and brown; ammonia changes the brown to green, and assumes itself the same colour (Brande). Chlorine throws down a blue precipitate from tincture of guaiacum. This precipitate is the *guaiaretic acid* of Jonas (*N. Br. Arch.* 69, 20); it has the property of rapidly turning fresh tincture of guaiacum blue. — *Strong nitric acid* dissolves guaiac resin, even in the cold, with evolution of nitric oxide and formation of a large quantity of oxalic acid and other substances (Brande). Dilute nitric acid turns the tincture blue when it contains nitrous acid only (Gmelin; Schacht). *Spiritus nitr. œther.* turns it blue immediately; the neutralised liquid only after a few minutes (Schacht). *Oil of vitriol* dissolves guaiac-resin, forming a fine dark-red solution, which is rendered violet by water, and violet-blue by alcohol, and carbonises when heated (Dulong; Trommsdorff; Schiff).

Guaiac-resin dissolves partially in aqueous *ammonia* to a brown liquid. — It dissolves still more easily in aqueous *alkalis* and their carbonates, forming red-green or brown-green solutions, which are precipitated by acids and by metallic salts.

With melted *caustic potash* and a little water, guaiac resin dissolves only when strongly heated, frothing up and forming a homogeneous mass, from which sulphuric acid throws down a black tar, and evolves an odour of volatile fatty acids, whilst protocatechuic acid (xvi, 236), or an acid of similar composition, and a second acid which turns alkalis green, remain in solution (Hlasiwetz & Barth).

On supersaturating the fused alkaline mass with dilute sulphuric acid, filtering from tar, and agitating with ether, these two acids are dissolved, and remain behind when the ether is evaporated. They are dissolved in water and precipitated with neutral acetate of lead; the washed precipitate is decomposed under warm water by hydrosulphuric acid; and the liquid is filtered and evaporated, whereupon procatechuic acid crystallises out, until the mother-liquor becomes brown and thick. After long standing, the mother-liquor solidifies to a friable mass, which is pressed, decolorised, and purified by repeated solution and solidification. — In this way a white, mealy powder, or on evaporating the alcoholic solution, a fissured varnish is obtained, containing, after drying at 150°, 64·75 p. c. C. and 6·39 H. This acid dissolves in water, alcohol, and ether : its solution in aqueous alkalis quickly assumes a dark emerald-green colour on exposure to the air ; sesquichloride of iron colours it olive-green, which is changed to a fine violet-red by soda. It reduces cold ammoniacal nitrate of silver, and the hot nitrate free from ammonia, also alkaline solutions of oxide of copper. Its red solution in oil of vitriol turns green on standing, yellowish-green on warming ; oxide of manganese colours it olive-green in the cold, and dirty-red on warming. The acid decomposes carbonates ; it is precipitated from its aqueous solution by neutral acetate of lead, the precipitate being soluble in acetic acid (Hlasiwetz & Barth).

Alcoholic *neutral acetate of lead* throws down from tincture of guaiacum a white precipitate, which quickly turns blue in sunshine; from the filtrate ammonia throws down a second precipitate (Johnston). An alkaline solution of the resin does not precipitate *acetate of copper* (Unverdorben). The tincture reduces *nitrate of silver* in the light (Johnston).

Guaiac resin dissolves abundantly in *alcohol*, with brown colour [and in *wood-spirit*, the solution turning blue in the same way as the alcoholic solution (Schönbein)] ; the tincture is rendered milky by water, and is precipitated by hydrochloric and sulphuric acids, but not by acetic acid. — It dissolves slowly but completely [only partially (Brande)] in ether Trommsdorff). — Dissolves completely in *fusel oil* and *amylic aldehyde*, and partially in *valerianic acid* and *valerianate of amyl* (Trantivein). Dissolves completely in *creosote* (Reichenbach). Cold *oil of turpentine* dissolves only a trace of guaiac-resin, the undissolved portion turning blue and then green (Trommsdorff); the hot liquid dissolves rather more, forming a colourless solution, which is coloured blue, red, and yellow on evaporation (Pfaff). — The resin is insoluble in *fat oils*.

*Addenda to the products from Guaiac-resin previously described.*

1. *To Guaiacene* (x, 411). — *Guaiol* of Völckel. Since investigated by Völckel (*Ann. Pharm.* 89, 348) and v. Gilm (*Ann. Pharm.* 106, 379).

After the distillate from guaiac resin has been subjected to fractional distillation, and the portion passing over below 120° is collected apart, this portion is to be repeatedly distilled off lime, till it ceases to be altered by cold caustic potash, and is no longer turned green by alcoholic sesquichloride of iron. It then forms a colourless, highly refractive, limpid liquid, boiling at 118°, and having a burning, aromatic

taste, and a powerful stupefying sweetish odour of bitter almonds. It contains 71·55 p. c. C., 9·82 H., and 18·63 O., corresponding to Deville's formula, $C^{10}H^8O^2$. — It is oxidised to oxalic acid by nitric acid, and to acetic acid by chromic acid. When warmed with solid caustic potash, it forms a brown resin, which is decolorised by melting the mass (without formation of angelic acid (x, 413). Guaiacene is insoluble in *ammonia-water*, and in cold solution of caustic *potash* of sp. gr. 1·25, and does not combine with *alkaline bisulphites* (v. Gilm). — Völckel examined impure guaiacene, to which he gave the formula $C^9H^7O^2$.

2. *Guaiacic acid* (xi, 397). Obtained from the resin in very small quantities only—about 1 decigramme from 4 pounds (Hadelich).

3. *Guaiacol or Pyroguaiacic acid* (xii, 350). — Guaiacol obtained by fractional distillation, and purified by Völckel's method (xii, 351, 2) is a mixture of two homologous oils of the formulæ $C^{14}H^8O^4$ and $C^{16}H^{10}O^4$, the latter of which may also be obtained from creosote (see xv, 161). By agitation with strong ammonia, or by the passage of ammonia-gas, it is converted into a slightly coloured crystalline mass, which is pressed, dissolved immediately in a little warm ether, and after cooling in a closed vessel, decomposed by strong alcoholic potash. Ammonia is thus liberated, and the whole solidifies to a white crystalline mass, which is again pressed, washed with ether, dried in a vacuum, and afterwards decomposed by aqueous oxalic acid or sulphuric acid. The oil thereby separated is washed, dried, and rectified. It is colourless, and has a very agreeable odour.

The oil heated to boiling in a retort yields, between 203° and 230°, products which have at first a greater density, and contain a smaller proportion of carbon and hydrogen, and afterwards, at a higher boiling-point, a lower specific gravity.

Specific gravity at 13° according to Hlasiwetz.

Portion at 210°          = 1·1171          Portion at 220°          = 1·0894
   „       „ 216—218°  = 1·1162             „        „ 220—225° = 1·0900
   „       „ 218°         = 1·1115

| | | Hlasiwetz. | | | | | |
|---|---|---|---|---|---|---|---|
| | | 205—210°. | 216—218. | 219—220°. | | | |
| 14 C ........ | 67·74 | .... 67·95 | .... 68·61 | .... 69·83 | 16 C ........ | 69·56 |
| 8 H ........ | 6·45 | .... 6·93 | .... 6·93 | .... 7·53 | 10 H ........ | 7·24 |
| 4 O ........ | 25·81 | .... 25·12 | .... 24·46 | .... 22·64 | 4 O ........ | 23·20 |
| $C^{14}H^8O^4$ .... | 100·00 | .... 100·00 | .... 100·00 | .... 100·00 | $C^{16}H^{10}O^4$ .... | 100·00 |

The potash-salt of the compound $C^{16}H^{10}O^4$ forms with *chloride of phenyl* an aromatic smelling oil, but no pyroguaiacin.

Both oils form compounds with ammonia and potash, the compound with the latter base, when prepared with oil of low boiling-point, having the composition $C^{14}H^7KO^4$. By treating crude guaiacol as above, and crystallising the product from alcohol, white potash-salts are produced, containing either ½ at., or, when an excess of caustic potash is employed, 1 at. of potassium to 16 at. of carbon.

| | Hlasiwetz. | | | | | Hlasiwetz. |
|---|---|---|---|---|---|---|
| $C^{14}H^7O^3$ | 58·03 | | $C^{16}H^9O^3$ | 60·84 | | |
| KO | 23·81 | .... 23·33 | KO | 22·17 | .... | 22·68 |
| 4 HO | 18·16 | .... 18·40 | 4 HO | 16·99 | | |
| $C^{14}H^7KO^4$ + 4aq. | 100·00 | | $C^{16}H^9KO^4$ + 4aq. | 100·00 | | |

The bi-acid salt contains 14·75 p. c. of potash, corresponding to the formula $C^{32}H^{19}KO^8$ + (2 aq) (calc. 14·15 p. c. KO). (Hlasiwetz.)

Guaiacol does not reduce moist oxide of silver (Schwanert).

<br>

*Oxy-azo-nucleus* $C^{40}NH^{19}O^8$.

# Hydroberberine.

$$C^{40}NH^{21}O^8 = C^{40}NH^{19}O^8,H^2.$$
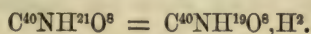
HLASIWETZ AND v. GILM. *Ann. Pharm. Suppl.* 2, 191.

*Preparation.* Six parts of berberine, 100 parts of water, 10 parts of oil of vitriol, and 20 parts of glacial acetic acid, together with a large quantity of granulated zinc, and a few pieces of platinum foil, are introduced into a capacious flask provided with an upright condenser, so that the condensed products may flow back into the flask. The contents of the flask are heated to the boiling-point, and kept at that temperature for an hour or two, or until the colour of the liquid has passed through dark gold-brown to light wine-yellow. The liquid is then filtered; any crystals that may have separated are dissolved in a little very dilute sulphuric acid; and the whole is precipitated with excess of ammonia. The yellowish-white precipitate thus produced is washed with water, dried, triturated, and repeatedly boiled with alcohol. The hydroberberine, which is difficultly soluble in alcohol, is deposited in crystals, partially during filtration, but chiefly after standing and concentration. The crystals are purified by oft-repeated crystallisation from alcohol; or, the solution containing zinc is mixed with an excess of a saturated solution of chloride of sodium, and the hydrochlorate of berberine thereby separated is decomposed by alcoholic ammonia. In this way ⅘ths of the berberine employed is obtained as hydroberberine.

*Properties.* Small colourless or yellowish needles, having an adamantine lustre, or long, flat needles of the monoclinic system. Does not lose weight at 100°.

| | | at 100°. | | | Hlasiwetz & v. Gilm. mean. | |
|---|---|---|---|---|---|---|
| 40 C | | 240 | ........ | 70·79 | ........ | 70·65 |
| N | | 14 | ........ | 4·13 | ........ | 4·14 |
| 21 H | | 21 | ........ | 6·19 | ........ | 6·50 |
| 8 O | | 64 | ........ | 18·89 | ........ | 18·71 |
| $C^{40}NH^{21}O^8$ | .... | 339 | ........ | 100·00 | ........ | 100·00 |

*Decompositions.* 1. Solutions of hydroberberine assume a yellow colour on standing in the *air*, or on prolonged boiling. — 2. *Dilute*

*nitric acid,* dropped into an alcoholic solution of the hydrochlorate, gradually forms berberine ; on heating the solution, red vapours are evolved. — 3. *Bromine* converts hydroberberine dissolved in bisulphide of carbon, into hydrobromate of berberine :

$$C^{40}NH^{21}O^8 + 4Br = C^{40}NH^{17}O^8,HBr + 3HBr.$$
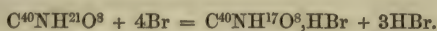
4. Hydroberberine dissolves in *oil of vitriol* with yellowish-green colour, which becomes darker on standing, and is changed to red-brown by chromic acid. — 5. *Iodide of ethyl* forms hydriodate of ethyl-hydroberberine.

*Combinations.* Hydroberberine is insoluble in *water.* — It combines with acids to form *mono-* and *bi-acid salts*, which are, for the most part, easily crystallisable. From their solutions ammonia and potash throw down the base in white flocks, which run together to a plaster in hot liquids.

*Phosphate of hydroberberine* forms large rhombic tables.

*Sulphate of Hydroberberine.* — A. *Mono-acid.* Prepared by heating very dilute sulphuric acid to the boiling point with excess of hydroberberine. From the solution, which still has an acid reaction, the salt is deposited in tufts of colourless, hair-like crystals, turning yellow when warmed, and losing their water of crystallisation over oil of vitriol, or more easily at 100°.

| | | Dried. | | | | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|---|---|
| 40 C | ............................. | 240 | ....... | 61·86 | ........ | 59·48 to 60·16 |
| N | ............................. | 14 | ....... | 3·61 | | |
| 22 H | ............... ............. | 22 | ....... | 5·67 | ........ | 5·80 ,,  6·10 |
| 9 O | ............................. | 72 | ....... | 18·55 | | |
| SO³ | ............................. | 40 | ....... | 10·31 | ........ | 11·21 ,, 12·68 |
| C⁴⁰NH²¹O⁸,HO,SO³ | .... | 388 | ........ | 100·00 | | |

It probably contained an admixture of the following salt.

B. *Sesqui-acid.* — A solution of hydroberberine in slight excess of dilute sulphuric acid, yields by spontaneous evaporation, large, transparent, very regular rhombohedrons, frequently accompanied by the salt A. The crystals are $2C^{40}NH^{21}O^8,3(HO,SO^3) + 8aq.$ ; they become dull and fissured in the air, and at a moderate temperature lose 8·27 p. c. of water (8 at. = 8·02 p. c.), and are converted into the lemon-yellow anhydrous salt. — At 100° it turns darker, and melts to a glassy mass, losing weight, and becoming insoluble in water. A solution of the salt in water deposits crystals of A.

| | | Air-dried. | | | | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|---|---|
| 80 C | ................................... | 480 | ....... | 53·50 | ........ | 53·48 |
| 2 N | ................................... | 28 | ....... | 3·15 | | |
| 53 H | ................................... | 53 | ....... | 5·90 | ........ | 5·93 |
| 27 O | ................................... | 216 | ....... | 24·08 | | |
| 3 SO³ | ...... ................................ | 120 | ....... | 13·37 | ........ | 13·16 |
| 2C⁴⁰NH²¹O⁸,3(HO,SO³) + 8aq. | .... | 897 | ........ | 100·00 | | |

| | Dried. | | | Hlasiwetz & v. Gilm. mean. | |
|---|---|---|---|---|---|
| 80 C | 480 | ... .... | 58·18 | ........ | 57·94 |
| 2 N | 28 | ........ | 3·39 | | |
| 45 H | 45 | ........ | 5·45 | ........ | 5·97 |
| 19 O | 152 | ........ | 18·43 | | |
| 3 SO³ | 120 | ........ | 14·55 | ........ | 14·49 |
| 2C⁴⁰NH²¹O⁸,3(HO,SO³) .... | 825 | ........ | 100·00 | | |

The salt contains 8 at., not 4 at. water; the dried salt 45 at., not 47 at. hydrogen, as erroneously stated in *Ann. Pharm. Suppl.* 2, 208 (Kr.).

C. *Bi-acid.* — Moderately dilute solutions of A and B are rendered turbid by excess of sulphuric acid, and, when more concentrated, deposit a tough resin, which, on standing, is converted into nodules of a bi-acid salt, crystallisable from absolute alcohol.

| | at 120°. | | | Hlasiwetz & v. Gilm. mean. | |
|---|---|---|---|---|---|
| 40 C | 240 | ........ | 54·92 | ....... | 54·73 |
| N | 14 | ........ | 3·22 | | |
| 23 H | 23 | ........ | 5·26 | ........ | 5·61 |
| 10 O | 80 | ........ | 18·30 | | |
| 2 SO³ | 80 | ........ | 18·30 | ........ | 18·59 |
| C⁴⁰NH²¹O⁸,2(HO,SO³) .... | 437 | ........ | 100·00 | | |

*Hydriodate of Hydroberberine.* — White, crystalline precipitate or colourless granules, precipitated by iodide of potassium from sulphate of hydroberberine. Very difficultly soluble in water.

| | at 120°. | | | Hlasiwetz & v. Gilm. mean. | |
|---|---|---|---|---|---|
| 40 C | 240 | ........ | 51·37 | ........ | 51·30 |
| N | 14 | ........ | 2·99 | | |
| 22 H | 22 | ........ | 4·71 | ........ | 5·02 |
| 8 O | 64 | ........ | 13·74 | | |
| I | 127 | ........ | 27·19 | ........ | 27·37 |
| C⁴⁰NH²¹O⁸,HI .... | 467 | ........ | 100·00 | | |

*Hydrobromate of Hydroberberine.* — Obtained in the same way as the preceding salt, which it resembles.

*Hydrochlorate of Hydroberberine.* — Hydroberberine in contact with hydrochloric acid gas, is converted into a white powder, which crystallises from hot water in laminæ. The easily formed solution of hydroberberine in warm dilute hydrochloric acid solidifies in the cold to a jelly, which is converted into difficultly soluble crystals on standing. The salt is precipitated from the sulphate by chloride of sodium; it dissolves in alcohol containing hydrochloric acid more easily than in water, and, on adding water to the solution till turbidity is produced, heating, and setting aside, the salt crystallises in small colourless tables or nodules.

| | at 100°. | | | Hlasiwetz & v. Gilm. | |
|---|---|---|---|---|---|
| 40 C | 240 | ........ | 63·91 | ........ | 63·70 |
| N | 14 | ........ | 3·73 | | |
| 22 H | 22 | ........ | 5·85 | ........ | 6·12 |
| 8 O | 64 | ........ | 17·06 | | |
| Cl | 35·5 | ........ | 9·45 | ........ | 9·44 |
| C⁴⁰NH²¹O⁸,HCl .... | 375·5 | ........ | 100·00 | | |

*Nitrate of Hydroberberine.* — Obtained with difficulty (on account of the oxidising action of the acid) by dissolving hydroberberine in nitric acid, or more easily in a pure state by mixing hot very dilute solutions of sulphate of hydroberberine and nitrate of soda. — Fine, iridescent laminæ or rhombic tables, drying up to a silvery pellicle.

|  |  | at 100°. |  |  |  | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|---|---|
| 40 C | .................... | 240 | ........ | 59·70 | ........ | 59·85 |
| 2 N | .................... | 28 | ........ | 6·96 | ........ | 7·02 |
| 22 H | .................... | 22 | ........ | 5·47 | ........ | 5·81 |
| 14 O | .................... | 112 | ........ | 27·87 | ........ | 27·32 |
| C⁴⁰NH²¹O⁸,HO,NO⁵ | .... | 402 | ........ | 100·00 | ........ | 100·00 |

*Chloroplatinate of Hydroberberine.* — Bichloride of platinum throws down from aqueous hydrochlorate of hydroberberine an abundant precipitate, which, when a hot alcoholic solution is employed, is obtained in orange-yellow crystals. — Dissolves with difficulty in water and alcohol, more easily in alcohol containing hydrochloric acid.

|  |  | at 100°. |  |  |  | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|---|---|
| 40 C | .................... | 240 | ........ | 44·03 | ........ | 43·93 |
| N | .................... | 14 | ........ | 2·56 |  |  |
| 22 H | .................... | 22 | ........ | 4·04 | ........ | 4·44 |
| 8 O | .................... | 64 | ........ | 11·74 |  |  |
| Pt | .................... | 98·5 | ........ | 18·07 | ........ | 18·14 |
| 3 Cl | .................... | 106·5 | ........ | 19·56 |  |  |
| C⁴⁰NH²¹O⁸,HCl,PtCl² | .... | 545·0 | ........ | 100·00 |  |  |

The *acetate* forms large tables and prisms; the *oxalate* small rhombic tables; the *tartrate* clusters of needles.

Hydroberberine dissolves in *alcohol*, more especially when hot. It dissolves in *bisulphide of carbon* and *chloroform* more easily than in cold alcohol, and crystallises from the solutions.

# Ethyl-hydroberberine.

$$C^{44}NH^{25}O^8 = C^{40}NH^{19}(C^4H^5)O^8,H^2.$$
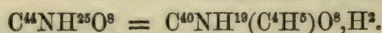
HLASIWETZ & v. GILM. *Ann. Pharm. Suppl.* 2, 191.

Obtained in combination with hydriodic acid by heating triturated hydroberberine with excess of iodide of ethyl in the water-bath, and crystallising the semi-fluid product from alcohol. — Pale yellow, rhombic prisms, brittle and bitter, soluble in hot, and less easily in cold water.

|  |  | Prisms. |  |  |  | Hlasiwetz & v. Gilm. |
|---|---|---|---|---|---|---|
| 44 C | .................... | 264 | ........ | 53·33 | ........ | 52·95 |
| N | .................... | 14 | ........ | 2·82 |  |  |
| 26 H | .................... | 26 | ........ | 5·25 | ........ | 5·52 |
| 8 O | .................... | 64 | ........ | 12·95 |  |  |
| I | .................... | 127 | ........ | 25·65 | ........ | 25·41 |
| C⁴⁰NH²⁰(C⁴H⁵)O⁸,HI | .... | 495 | ........ | 100·00 |  |  |

# Papaverine.

$$C^{40}NH^{21}O^8 = C^{40}NH^{19}O^8, H^2.$$
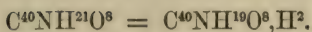
G. Merck. *Ann. Pharm.* 66, 125 ; *Pharm. Centr.* 1848, 939 ; *N. Br. Arch.* 56, 312 ; *N. J. Pharm.* 15, 167. — *Ann. Pharm.* 73, 50 ; *Pharm. Centr.* 1850, 52.

Anderson. *Trans. Roy. Soc. Edinb.* 21, 1, 195 ; *Chem. Gaz.* 1855, 21 ; *Ann. Pharm.* 94, 235 ; *Pharm. Centr.* 1855, 279 ; *J. pr. Chem.* 65, 233.

Discovered in 1848 by Merck, in opium.

*Preparation.* An aqueous extract of opium is precipitated with caustic soda ; the precipitate, consisting chiefly of morphine, is treated with alcohol ; the brown tincture thereby obtained is evaporated ; and the residue is mixed with a little ammonia, whereby (at first) a brown resinous precipitate is produced. This is dissolved in dilute hydrochloric acid, and mixed with acetate of potash, which separates a dark resin. This last body is washed with water and boiled with ether, from which papaverine crystallises on cooling. — A simpler plan is to dry the brown resin over the water-bath, and add to it an equal quantity of alcohol, whereby a thick syrup is produced, which solidifies in a crystalline mass on standing for some days. The crystals are pressed, and purified by recrystallisation from alcohol with the help of animal charcoal. The papaverine thus obtained contains narcotine, which is removed by dissolving the crystals in hydrochloric acid and recrystallising the hydrochlorate (Merck).

Anderson prepares papaverine from the black mother-liquor obtained in the preparation of morphine, codeine, &c., according to xvi, 420, as follows : 1. *From narcotine containing papaverine.* When this substance is crystallised repeatedly from boiling alcohol, the more easily soluble papaverine remains in the mother-liquors and crystallises therefrom mixed with narcotine. The crystals last obtained are triturated and treated repeatedly with small quantities of acetic acid so long as the acid is completely neutralised, and the filtered solutions are precipitated with ammonia (or caustic potash). The precipitate thus obtained must be crystallised from boiling alcohol, as otherwise it retains a large quantity of ammonia (*Chem. Soc. Qu. J.* 15, 466). — 2. *From the precipitate thrown down by basic acetate of lead, and containing resin, narcotine, and papaverine.* The precipitate is boiled with alcohol ; the alcohol is evaporated ; the residue is dissolved in hydrochloric acid ; and the solution, filtered from resin, is left to crystallise, whereupon hydrochlorate of papaverine separates, whilst hydrochlorate of narcotine remains in the mother-liquor. — 3. Papaverine is also obtained in the preparation of opianyl (Meconin) according to xiv, 423.

*Properties.* Papaverine crystallises from alcohol in confused masses of white needles. Its solutions scarcely restore the colour of reddened litmus. It has no particular action on the organism (Merck). Its rotatory action on polarised light is but slight, and on account of the difficult solubility of papaverine, cannot be determined with certainty (Bouchardat & Boudet, *N. J. Pharm.* 23, 192.)

|  |  |  |  |  | | Merck. | | Anderson. mean. |
|---|---|---|---|---|---|---|---|---|
| 40 C | ............ | 240 | ........ | 70·79 | ........ | 70·59 | ........ | 70·63 |
| N | ............ | 14 | ........ | 4·13 | ........ | 4·75 | ........ | 4·17 |
| 21 H | ............ | 21 | ........ | 6·20 | ........ | 6·53 | ........ | 6·40 |
| 8 O | ............ | 64 | ........ | 18·88 | ........ | 18·13 | ........ | 18·80 |
| C⁴⁰NH²¹O⁸.... | | 339 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Isomeric with hydroberberine.

*Decompositions.* 1. Papaverine assumes a purple [deep blue (Merck)] colour with *oil of vitriol* (Anderson ; Guy). Permanganate of potash colours the solution green, then slate-grey (Guy, *Anal. Zeitschr.* 1, 93). — 2. It dissolves in dilute *nitric acid* without decomposition, but on warming the solution with excess of strong nitric acid, it acquires a dark-red colour, evolves red fumes, and deposits orange-coloured crystals of nitrate of nitropapaverine (Merck ; Anderson). — 3. *Bromine-water*, dropped into hydrochlorate of papaverine, produces hydrobromate of bromopapaverine (Anderson). — 4. *Chlorine*, passed into a solution of hydrochlorate of papaverine, turns it brown and throws down a dirty-grey precipitate, a solution of which in boiling alcohol deposits, on cooling, the hydrochlorate of a chlorinated base in the form of a resin (Anderson). — 5. Papaverine heated with *soda-lime*, evolves a volatile base, probably propylamine or ethylamine, the platinum-salt of which contains 36·21 p. c. of platinum (Anderson). — 6. Papaverine turns brown when heated with *peroxide of manganese* (or *peroxide of lead*), sulphuric acid, and water, and after boiling for some hours deposits brown crystalline flocks, which dissolve in alcohol, and also in water when washed therewith, and are precipitated from the aqueous solution by sulphuric acid (Merck). — 7. Papaverine heated with *iodide of ethyl* yields hydriodate of papaverine without forming ethyl-papaverine. The reaction is attended either by the formation of alcohol :—

$$C^{40}NH^{21}O^8 + C^4H^5I + 2HO = C^{40}NH^{21}O^8,HI + C^4H^6O^2.$$
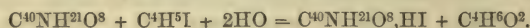
or (since a portion of the papaverine is converted into hydriodate even in the absence of water) by the formation of ether :—

$$C^{40}NH^{21}O^8 + C^4H^5I + C^4H^6O^2 = C^{40}NH^{21}O^8,HI + 2C^4H^5O.$$
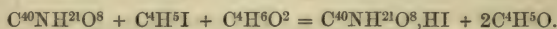
(How, *Trans. Roy. Soc. Edinb.* 21, 1, 27 ; *Ann Pharm.* 92, 336.)

*Combinations.* Papaverine does not dissolve in *water*. Its *salts* are for the most part difficultly soluble in water (Merck).

*Carbonate of papaverine* is prepared in the same way as carbonate of morphine, by precipitating the hydrochlorate with carbonate of silver, and not by precipitation with alkaline carbonates (How, *Chem. Gaz.* 1854, 341).

*Sulphate of papaverine* is crystallisable (Merck). — The *hyposulphite* is soluble and is obtained by the action of hydrosulphate of ammonia, in the same way as the morphine salt (xvi, 430) (How).

*Papaverine and Iodine.* — a. *With 3 at. Iodine.* — Crystallises after some time from tincture of iodine to which papaverine has been added.

— Small rectangular prisms, dark-red by transmitted, purple-red by reflected light. — Not altered by dilute acids, but decomposed by ammonia or potash, with separation of papaverine. Insoluble in water. Soluble in boiling alcohol (Anderson).

|  |  |  |  |  | Anderson. |
|---|---|---|---|---|---|
| 40 C | ............... | 240 | ........ | 33·33 | ........ 33·02 |
| N | ............... | 14 | ........ | 1·95 |  |
| 21 H | ............... | 21 | ........ | 2·92 | ........ 3·21 |
| 8 O | ............... | 64 | ........ | 8·88 |  |
| 3 I | ............... | 381 | ........ | 52·92 | ........ 52·90 |
| $C^{40}NH^{21}O^{8},3I$ | ........ | 720 | ........ | 100·00 |  |

b. *With 5 at. Iodine.* — By evaporating the mother-liquor of the preceding salt, crystals are obtained, which separate from alcohol in thin reddish needles, appearing orange-coloured by transmitted light. — Evolves iodine when heated over 100°. Rapidly decomposed by ammonia (Anderson).

|  |  |  |  |  | Anderson. |
|---|---|---|---|---|---|
| 40 C | ............... | 240 | ........ | 24·64 | ........ 24·78 |
| N | ............... | 14 | ........ | 1·43 |  |
| 21 H | ............... | 21 | ........ | 2·15 | ........ 2·59 |
| 8 O | ............... | 64 | ........ | 6·57 |  |
| 5 I | ............... | 635 | ........ | 65·21 | ........ 64·60 |
| $C^{40}NH^{21}O^{8},5I$ | ........ | 974 | ........ | 100·00 |  |

*Hydriodate of Papaverine.* — Papaverine dissolves in a mixture of alcohol and iodide of ethyl, partially in the cold, and completely when heated in the water-bath; on concentrating the solution, crystals of hydriodate of papaverine are obtained. (See above.) Colourless rhombic crystals, which turn brown at 100°, with loss of weight, and afterwards throw down a brown resin when dissolved in hot water. Dissolves easily in boiling water, the solution becoming milky on cooling and depositing oily drops, which afterwards solidify in needles. Soluble in alcohol, but in absolute alcohol the crystals dissolve only on boiling (How).

|  |  |  |  |  | How. |
|---|---|---|---|---|---|
| $C^{40}NH^{22}O^{8}$ | ............... | 340 | ........ | 72·8 |  |
| I | ............... | 127 | ........ | 27·2 | ........ 27·02 |
| $C^{40}NH^{21}O^{8},HI$ | ........ | 467 | ........ | 100·0 |  |

*Hydrochlorate of Papaverine.* — Papaverine dissolves easily in dilute hydrochloric acid, and is precipitated from the solution by a larger quantity of hydrochloric acid in the form of a thick heavy oil. On standing for some time, crystals form in the oil, as well as in the supernatant liquid, so that the oily layer is converted at last into a heap of short needles (Merck). Right prismatic, hemihedral. Rhombic prism *y* (fig. 53) having the obtuse lateral edges slightly truncated by *p*, the bevelling faces *u* resting on the acute lateral edges, and the octahedron *α* being hemihedrally developed. *y* : *y* over *p* = 100° (Kopp); *u* : *u* above = 119° 20′ (Kopp); *α* : *u* = 149° 15′ (Pasteur); Kopp, *Ann. Pharm.* 66, 127. — Pasteur, *N. Ann. Chim. Phys.* 38, 456. Very slightly soluble in cold water (Merck).

|         |        | at 100°. |         |        |         | Merck. |
| ------- | ------ | -------- | ------- | ------ | ------- | ------ |
| 40 C    | ....   | 240      | ........ | 63·91  | ........ | 63·74  |
| N       | ....   | 14       | ........ | 3·72   |         |        |
| 22 H    | ....   | 22       | ........ | 5·86   | ........ | 6·07   |
| 8 O     | ....   | 64       | ........ | 17·03  |         |        |
| Cl      | ....   | 35·5     | ........ | 9·48   | ........ | 9·42   |

$C^{40}NH^{21}O^8,HCl$ .... 375·5  ........ 100·00

*Nitrate of Papaverine.* — A hot solution of the hydrochlorate is decomposed by nitrate of silver: the filtrate crystallises on cooling. — It is not obtained pure by treating papaverine with nitric acid, as the slightest excess of acid colours the solution yellow (Merck).

|         |        |       |         |       |         | Merck. |
| ------- | ------ | ----- | ------- | ----- | ------- | ------ |
| 40 C    | ....   | 240   | ........ | 59·70 | ........ | 60·94  |
| 2 N     | ....   | 28    | ........ | 6·96  |         |        |
| 22 H    | ....   | 22    | ........ | 5·47  | ........ | 6·21   |
| 14 O    | ....   | 112   | ........ | 27·87 |         |        |

$C^{40}NH^{21}O^8,HO,NO^5$ .... 402  ........ 100·00

*Iodomercurate of potassium* precipitates papaverine, even from very dilute solutions, yellowish-white and amorphous (Delffs).

*Chloroplatinate of Papaverine.* — Aqueous hydrochlorate of papaverine produces with bichloride of platinum a yellow pulverulent precipitate, insoluble in water and alcohol (Merck).

|         |        | at 100°. |         |       |         | Merck. |
| ------- | ------ | -------- | ------- | ----- | ------- | ------ |
| 40 C    | ....   | 240      | ........ | 44·02 | ........ | 43·71  |
| N       | ....   | 14       | ........ | 2·57  |         |        |
| 22 H    | ....   | 22       | ........ | 4·04  | ........ | 4·55   |
| 8 O     | ....   | 64       | ........ | 11·74 |         |        |
| Pt      | ....   | 98·7     | ........ | 18·10 | ........ | 17·82  |
| 3 Cl    | ....   | 106·5    | ........ | 19·53 |         |        |

$C^{40}NH^{21}O^8,HCl,PtCl^2$ .... 545·2  ........ 100·00

Papaverine dissolves with difficulty in cold *alcohol* and *ether*, but more easily in the hot liquids (Merck).

*Oxynitrazo-nucleus* $C^{40}NXH^{18}O^8$

## Nitropapaverine.

$$C^{40}N^2H^{20}O^{12} = C^{40}NXH^{18}O^8,H^2.$$
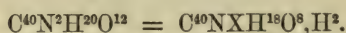
ANDERSON. *Trans. Roy. Soc. Edinb.* 21, 1, 195; *Ann. Pharm.* 94, 237.

On adding to a solution of papaverine in dilute nitric acid an excess of concentrated nitric acid, the liquid assumes a dark-red colour, evolves red vapours, and deposits orange-coloured crystals of nitrate of nitropapaverine. The crystals are decomposed by boiling aqueous ammonia, and the flocks which separate are crystallised from boiling alcohol.

Pale reddish-yellow needles, which give off 2·29 p. c. of water (= 1 at.) when heated. Has an alkaline reaction.

| | Dried. | | | | Anderson. |
|---|---|---|---|---|---|
| 40 C | ...................... | 240 | ........ | 62·50 | ........ | 62·31 |
| 2 N | ...................... | 28 | ........ | 7·29 | | |
| 20 H | ...................... | 20 | ........ | 5·20 | ........ | 5·21 |
| 12 O | ...................... | 96 | ........ | 25·01 | | |
| $C^{40}NXH^{20}O^8$ | ........ | 384 | ........ | 100·00 | | |

Nitropapaverine melts when *heated*, and afterwards explodes. — With *oil of vitriol* it exhibits the purple coloration of papaverine. — When heated with boiling strong *caustic potash*, it evolves traces of a volatile base.

Nitropapaverine is insoluble in *water*. — It neutralises *acids* completely, forming pale reddish-yellow salts, but little soluble in water. From solutions of the salts, ammonia precipitates the base in pale-yellow flocks.

*Sulphate of Nitropapaverine* forms small prisms, slightly soluble in water; the *hydrochlorate*, pale-yellow needles, little soluble in water, but easily soluble in aqueous hydrochloric acid and in alcohol.

*Nitrate of Nitropapaverine.* — Yellow four-sided tables, orange-yellow in an impure state. Very slightly soluble in cold, and but little more so in boiling water; easily soluble in aqueous acids and in alcohol and ether.

| | Crystals. | | | | Anderson. |
|---|---|---|---|---|---|
| 40 C | .............................. | 240 | ........ | 53·69 | ........ | 53·68 |
| 3 N | .............................. | 42 | ........ | 9·38 | | |
| 21 H | .............................. | 21 | ........ | 4·69 | ........ | 4·95 |
| 18 O | .............................. | 144 | ........ | 32·24 | | |
| $C^{40}NXH^{20}O^8,HO,NO^5$ | .... | 447 | ........ | 100·00 | | |

*Chloroplatinate of Nitropapaverine.* — Pale-yellow precipitate.

| | | | | | Anderson. |
|---|---|---|---|---|---|
| 40 C | .............................. | 240 | ........ | 40·66 | ........ | 40·47 |
| 2 N | .............................. | 28 | ........ | 4·72 | | |
| 21 H | .............................. | 21 | ........ | 3·55 | ........ | 3·80 |
| 12 O | .............................. | 96 | ........ | 16·26 | | |
| 3 Cl | .............................. | 106·5 | ........ | 18·09 | | |
| Pt | .............................. | 98·7 | ........ | 16·72 | ........ | 16·56 |
| $C^{40}NXH^{20}O^8,HCl,PtCl^2$.... | | 590·2 | ........ | 100·00 | | |

Nitropapaverine dissolves in *alcohol* and in *ether*.

*Oxybromazo-nucleus* $C^{40}NBrH^{18}O^8$.

## Bromopapaverine.

$$C^{40}NBrH^{20}O^8 = C^{40}NBrH^{18}O^8,H^2.$$
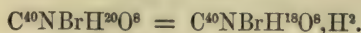
ANDERSON. *Trans. Roy. Soc. Edinb.* 21, 1, 195; *Ann. Pharm.* 94, 238.

Bromine-water is dropped into aqueous hydrochlorate of papaverine

till the precipitate of hydrobromate of bromopapaverine, which disappears again at first, remains permanent. The precipitate is decomposed by ammonia, and the bromopapaverine is crystallised from boiling alcohol.

Small white needles.

|  |  |  |  |  | Anderson. |  |
|---|---|---|---|---|---|---|
| 40 C | .................. | 240 | ........ | 57·41 | ........ | 57·23 |
| N | .................. | 14 | ........ | 3·34 | | |
| 20 H | .................. | 20 | ........ | 4·78 | ........ | 5·02 |
| 8 O | .................. | 64 | ........ | 15·34 | | |
| Br | .................. | 80 | ........ | 19·13 | ........ | 19·45 |
| $C^{40}NBrH^{20}O^8$ | ........ | 418 | ........ | 100·00 | | |

Bromopapaverine is insoluble in *water*.

*Hydrobromate of Bromopapaverine.* — (See above.) Yellow precipitate, deposited from boiling alcohol as a crystalline powder. — Melts and decomposes when heated. Insoluble in water.

|  |  |  |  |  | Anderson. |  |
|---|---|---|---|---|---|---|
| 40 C | .................. | 240 | ........ | 48·09 | ........ | 48·36 |
| N | .................. | 14 | ........ | 2·80 | | |
| 21 H | .................. | 21 | ........ | 4·20 | ........ | 4·35 |
| 8 O | .................. | 64 | ........ | 12·85 | | |
| 2 Br | .................. | 160 | ........ | 32·06 | ........ | 32·48 |
| $C^{40}NBrH^{20}O^8$ | ........ | 499 | ........ | 100·00 | | |

*Hydrochlorate of bromopapaverine* dissolves slightly in water.

Bromopapaverine dissolves easily in *alcohol* and *ether*.

*Oxy-azo-nucleus*  $C^{40}N^2H^{22}O^4$.

# Quinine.

$$C^{40}N^2H^{24}O^4 = C^{40}N^2H^{22}O^4,H^2.$$
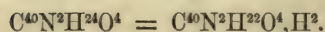
*On Cinchonine and Quinine :*

PELLETIER & CAVENTOU. *Ann. Chim. Phys.* 15, 291 and 337 ; *Schw.* 32, 413 ; 33, 62 ; *J. Pharm.* 7, 49.
GEIGER. *Repert.* 11, 79. — *Mag. Pharm.* 7, 41.
BUCHNER. *Repert.* 12, 1.
PELLETIER & DUMAS. *Ann Chim. Phys.* 24, 169 ; *Mag. Pharm.* 5, 164 and 243.
BAUP. *Ann. Chim. Phys.* 27, 323 ; *Schw.* 43, 471 ; *N. Tr.* 10, 2, 130.
O. HENRY & PLISSON. *J. Pharm.* 13, 268 and 369 ; *N. Tr.* 15, 2, 59 and 16, 1, 200 ; *Berl. Jahrb.* 29, 2, 113.
DUFLOS. *Schw.* 42, 306.
MERCK. *N. Tr.* 20, 1, 134.
LIEBIG. *Pogg.* 21, 23. — *Ann. Pharm.* 26, 47 ; 29, 63.
REGNAULT. *Ann. Pharm.* 26, 11 ; *J. pr. Chem.* 16, 258. — *Ann. Pharm.* 29, 58.

LAURENT. *N. Ann. Chim. Phys.* 19, 363; *Ann. Pharm.* 62, 98; *J. pr. Chem.* 40, 403; *Kopp's Jahresber.* 1847 and 1848, 615.

PASTEUR.  *Compt. rend.* 36, 26; *N. J. Pharm.* 23, 123; *J. pr. Chem.* 58, 376; *Pharm. Centr.* 1853, 95; *Ann. Chim. Phys.* 38, 437; *Compt. rend.* 37, 110; *N. J. Pharm.* 24, 161; *J. pr. Chem.* 60, 129; *Ann. Pharm.* 88, 209; *Chem. Gaz.* 1853, 321. — *Compt. rend.* 37, 162; *J. pr. Chem.* 60, 134; *Ann. Pharm.* 88, 211; *Chem. Gaz.* 1853, 401. Abstract of the whole of the memoirs: *Kopp's Jahresber.* 1853, 419.

SCHÜTZENBERGER.  *Compt. rend.* 46, 894; *J. pr. Chem.* 74, 76. — *Compt. rend.* 46, 1065; *J. pr. Chem.* 74, 227; *Ann. Pharm.* 108, 347; *Chem. Centr.* 1858, 541. — *Compt. rend.* 47, 81; *J. pr. Chem.* 75, 124; *Ann. Pharm.* 108, 350; *Chem. Centr.* 1858, 678; *Compt. rend.* 47, 233; *J. pr. Chem.* 75, 125; *Ann. Pharm.* 108, 351; *Chem. Centr.* 1858, 677. — *Compt. rend.* 47, 235; *J. pr. Chem.* 75, 254; *Ann. Pharm.* 108, 353; *Chem. Centr.* 1858, 684.  Abstract of the whole of the memoirs: *Kopp's Jahresber.* 1858, 369.

*On Quinine alone:*

ROBIQUET.  *Ann. Chim. Phys.* 17, 316; *N. Tr.* 6, 2, 30.

STRATINGH.  *Scheikund. Verhandl.* Gröningen, 1822; abstr. *Repert.* 15, 139.

PELLETIER.  *J. Pharm.* 11, 249; *N. Tr.* 11, 2, 140.

DUFLOS.  *Berl. Jahrb.* 27, 1, 100.

STRECKER.  *Ann. Pharm.* 91, 155; abstr. *J. pr. Chem.* 62, 445; *Pharm. Centr.* 1854, 661; *N. Ann. Chim. Phys.* 42, 369; *Compt. rend.* 39, 59; *Phil. Mag.* [4], 8, 123; *Kopp's Jahresber.* 1854, 505.

*Cinchona-resin* of the older chemists.  *Chinin.*

Fourcroy (*Ann. Chim.* 8, 113; 9, 7) distinguished in cinchona-barks a peculiar *resinous extractive*, which Vauquelin (*Ann. Chim.* 59, 130 and 148) prepared in a purer form as *Chinastoff*.  The same substance was obtained in a still purer state by Gomez (*Edinb. Med. and Surg. J.* 1811, art. 420) and Pfaff (*Schw.* 10, 265).

Pelletier & Caventou showed that the substance was of a twofold nature, and consisted of quinine or cinchonine, according to the kind of bark from which it was extracted.  They showed further that the brown or grey cinchona-barks contain a large quantity of cinchonine with very little quinine; that Royal bark contains a large quantity of quinine, with very little cinchonine, whilst the red bark contains the two substances in about equal proportions.  Guided by Sertürner's discovery of the existence of organic salt-bases, they established the basic nature of these substances, rendered very probable by previous investigations, and investigated their compounds more exactly.

Schützenberger (*Compt. rend.* 47, 235) supposes the existence of a second quinine, to which, from analyses of the substance itself and of its platinum-salt and benzoyl-derivatives, he assigns the formula $C^{42}N^2H^{28}O^4$.  When this quinine is precipitated from its acid solution by ammonia, the liquid deposits, on standing for some time, scales composed of long needles, larger than the needles of ordinary quinine. A third quinine is said to form flat laminæ.

*Source.*  In the barks of various species of *Cinchona*, accompanied in all cases by larger or smaller quantities of cinchonine, and in some

instances also by quinidine and cinchonidine. The different kinds of bark contain, on an average, the following quantities of quinine and cinchonine :

### 1. Brown or grey barks.

| | | |
|---|---|---|
| Huanoco ............... | 0·40 p. c. quinine, | 1·70 p. c. cinchonine. |
| Loxa ...................... | 0·35 ,, ,, | 0·34 ,, ,, |
| Pseudoloxa ........... | 0·35 ,, ,, | 0·66 ,, ,, |
| Huamalies ............ | 0·30 ,, ,, | 0·85 ,, ,, |
| Jaen pallida ............ | 0·56 ,, ,, | 0·60 ,, ,, |

### 2. Yellow or orange barks.

Royal or Calisaya bark.

| | | |
|---|---|---|
| a. plana ................................. | 2·2  p. c. quinine, | 0·28 p. c. cinchonine. |
| b. convoluta ............................ | 1·1 ,, ,, | 0·42 ,, ,, |
| Cinchona flava fibrosa ........ | 1·05 ,, ,, | 0·83 ,, ,, |
| Cinchona flava dura ........... | 0·54 ,, ,, | 0·48 ,, ,, |
| Pitayo .................................... | 1·68 ,, ,, | 0·90 ,, ,, |

### 3. Red bark.

| | | |
|---|---|---|
| Cinchona rubra   ................ | 0·91 p. c. quinine, | 1·05 p. c. cinchonine. |

According to M'Ivor, a covering of moss on the bark during its growth increases the percentage of the alkaloïds, and this observation has been confirmed by De Vrij, who found in a young bark covered with moss, 8·4 p. c. of alkaloïds.

For fuller statements see *Handbuch* viii. [2], 50, and Watts's *Dictionary of Chemistry* i, 970 ; also tables of the percentage of alkaloïds in cinchona-barks, by Pfaff (*Berger's Monographie der Chinarinden, J. Chim. méd.* 16, 192), Winckler (*Repert.* 75, 323), Guillermond (*N. J. Pharm.* 44, 124 ; *Pharm. Viertelj.* 13, 432 ; *Chem Centr.* 1864, 239), Wigand & Dronke (*N. Br. Arch.* 115, 231) ; for a summary of the earlier statements, see *Handwörterbuch*, 2nd ed. 2, [2] 989. — See also Karsten (*Berl. Acad. Ber.* 1858, 260 ; *J. pr. Chem.* 74, 66 ; *Kopp's Jahresber* 1858, 364), who found the percentage of alkaloïds in the same kind of bark to vary greatly with its age and locality. — Concerning East Indian barks, see Howard (*N. Br. Arch.* 115, 249), De Vrij (*N. Jahrb. Pharm,* 14, 243 ; and further *Pharm. Trans.*, 5, 593 ; 6, 15 ; *Pharm. Viertelj.* 14, 221 and 227). The leaves of cinchona, especially the older leaves, contain quinine (Anderson, *Pharm. Viertelj.* 13, 593) ; the roots are richer in alkaloïds than the bark and contain as much as 8·66 p. c. (De Vrij).

*Preparation of Cinchonine and Quinine.* — Any one of the true cinchona-barks is boiled with water containing a little sulphuric or hydrochloric acid ; it is then pressed between linen cloth, and the residue is boiled with fresh quantities of acidulated water so long as the liquid acquires a bitter taste. The united decoctions, which contain sulphate or hydrochlorate of quinine and cinchonine, together with colouring matter, tannin, cinchona-red, kinic acid, quinidine, cinchonidine, and lime, are clarified, either by allowing them to deposit and decanting the clear liquid, or by filtration, and after partial evaporation, are mixed with sufficient ammonia, potash, or soda to produce a slight alkaline reaction. Or better, since an excess of these alkalis dissolves the bases, the liquid is boiled with excess of lime (or magnesia) ; the cold liquid is thrown upon a filter ; and the residue is washed with a little cold water and dried. This residue consists of impure quinine and cinchonine, and where lime or magnesia is employed, the excess of

these bases, intimately combined with colouring matter, tannin, and cinchona-red, and where sulphuric acid and lime are used, together also with sulphate of lime. It is exhausted several times with boiling alcohol of sp. gr. 0·84 (and in the case of quinine also with weaker alcohol); the liquid is filtered hot; the filtrate is distilled to remove the greater part of the alcohol; and the residue, which still contains cinchona-red and other colouring matters, is neutralised with sulphuric acid and evaporated to crystallisation, whereupon the greater part of the sulphate of quinine crystallises out, whilst a portion remains in the mother-liquor, together with sulphate of cinchonine and a brown substance. The mother-liquor, separated from the crystals as far as possible, is precipitated with carbonate of soda; the precipitate is dissolved in alcohol, and the solution is evaporated, whereupon crystals of cinchonine are obtained.

*A special mode of preparation.* — One kilogramme of coarsely powdered calisaya bark is steeped in water containing 60 grammes of hydrochloric acid, and on the following day the liquid is heated to boiling and boiled for two hours. A second and a third decoction are made, with addition of 30 grammes of hydrochloric acid each time, and a fourth decoction, made without any addition of acid, serves to exhaust fresh bark. The hot acid decoctions are mixed with a slight excess of carbonate of soda; the precipitate thereby formed is collected on a close linen filter, pressed, dried, triturated, and treated five or six times with warm alcohol of 85°; and the tincture is exactly neutralised with sulphuric acid, filtered, and partially distilled: the residue then solidifies in a crystalline mass on cooling. The crystals, after being freed from the black mother-liquor by pressing, are suspended in warm water, mixed with half their weight of bone-black, and set aside for a day: they are then dissolved in 25 parts of boiling water, and the solution is filtered: on cooling, it deposits sulphate of quinine in fine white crystals (*N. J. Pharm.* 45, 236).

*Purification of Quinine and Cinchonine.* — 1. Sulphate of quinine may be obtained white by repeated crystallisation, the colouring matters remaining in the mother-liquors. — 2. Animal charcoal, purified by acids, removes from the aqueous solutions of both salts a large quantity of brown colouring matter. — 3. On precipitating the sulphates by excess of lime, boiling the dried precipitate with alcohol, and filtering, a large quantity of colouring matter remains with the lime. — 4. When the impure quinine or cinchonine remaining from the distillation of the alcoholic solution, is neutralised with hydrochloric or acetic acid, and mixed in the former case with protochloride of tin, or in the latter with neutral acetate of lead, compounds of the oxides of these metals with colouring matter are precipitated. From the filtrate the excess of metallic salt is removed by means of hydrosulphuric acid or by hydrosulphate of an alkali not in excess; and the quinine and cinchonine, in a purer state, are then precipitated by alkalis. — 5. Hydrate of alumina, formed by adding alum to aqueous solutions of the sulphates, and precipitating with somewhat less than an equivalent quantity of carbonate of potash, carries down with it a large quantity of colouring matter. — 6. Cinchonine may be purified by recrystallisation from hot alcohol, the colouring matter remaining in the mother-liquor, according to Stoltze, more especially in presence of a little ammonia,

*Separation of Quinine and Cinchonine.* — 1. Sulphate of quinine is much less soluble in water and far more easily crystallisable than sulphate of cinchonine, which remains in the mother-liquor. — 2. Quinine is much more easily soluble than cinchonine in cold alcohol, so that the greater part of the latter substance crystallises from a hot saturated solution of the two, whilst the whole of the quinine remains in solution with a little cinchonine. From a mixture of the two alkaloïds, cold weak alcohol takes up almost exclusively quinine. — 3. Quinine is much more freely soluble than cinchonine in ether.

Commercial sulphate of quinine, even from the best works, contains traces of quinidine or similar bases. De Vrij and Alluard (*N. J. Pharm.* 46, 194) purify it by converting into sulphate of iodoquinine, which salt, on account of its low solubility, admits of easy separation from foreign bases. They decompose the sulphate of iodoquinine with aqueous hydrosulphuric acid, precipitate the cold aqueous solution with caustic soda, wash the soft resinous precipitate of quinine, and dry it, first in the air, then over the water-bath ; it then becomes hard and friable.

Amongst numerous other methods of preparation the following peculiarities occur :—

a. *Exhaustion of the bark.* — To get rid, as far as possible, of tannin, colouring matter, cinchona-red, and kinic acid, Badollier (*Ann. Chim. Phys.* 17, 273) first boils the bark with water containing potash, and rejects this decoction. Cassola (*J. Pharm.* 15, 167 ; *Br. Arch.* 30, 298), and Scharling (Pogg. 24, 182) and lately also Herring (*Dingl.* 132, 211 ; *J. pr. Chem.* 62, 505) proceed in a similar manner. This plan, however, must occasion a loss of quinine and cinchonine, seeing that they are soluble to a slight extent in alkalis (Stoltze), unless the alkaloïds be recovered from the alkaline decoction, as in Herring's process. Gilbert exhausts the bark with ammonia ; Stoltze (*Schw.* 43, 457) and Bischoff (*Mag. Pharm.* 27, 135) with lime-water, from which the latter chemist recovers the kinic acid.

In the foregoing processes, the quantity of hydrochloric or sulphuric acid used in the extraction of the bark, amounts, at most, to 3 or 5 per cent. of the weight of the bark. Processes are given, however, with quantities of acid varying from 1 to 30 per cent. When too much acid is used, the excess may be removed by means of chalk, whereby a large quantity of colouring matter is precipitated. Henry employs also wood-vinegar for the extraction ; Stratingh a mixture of sulphuric and hydrochloric acids, so that less sulphate of lime may be formed afterwards. O. Henry (*J. Pharm.* 21, 212 ; *Ann. Pharm.* 15, 300) exhausts with alcohol containing sulphuric acid ; Veltmann (*Schw.* 54, 381) with alcohol containing hydrochloric acid. — Inasmuch as acids at boiling heat dissolve a large quantity of foreign matters from the bark, Stoltze recommends cold extraction in a percolator, or exhaustion at 50°. In the cold, six times repeated exhaustion is necessary.

b. *Precipitation.* Hermann (*Mag. Pharm.* 25, 71) recommends the addition of protochloride of tin, to remove colouring matter before precipitating the bases. Pelletier & Caventou decolorise the mother-liquors with neutral acetate of lead, and Stratingh employs alum for the same purpose. See purification 4 and 5 (p. 265). — Hydrate of lime is generally employed as the precipitant. By its use, however, as well as by the

use of potash, and more particularly of ammonia, a loss of substance is incurred, in consequence of the solubility of quinine in lime-water and chloride of calcium. This loss may be prevented by the employment of caustic soda (Calvert, *N. J. Pharm.* 2, 388). Or, after adding the hydrate of lime, the liquid is filtered as soon as it exhibits an alkaline reaction (Henry). Geiger precipitates with a large excess of carbonate of soda, in which quinine is nearly insoluble, whilst a large quantity of colouring matter remains in solution.

c. *Further treatment of the Precipitate.* After precipitating with lime, the precipitate must not be exposed to the air, lest by the action of carbonic acid on the lime-compound, some of the colouring matter may be rendered soluble (Franquinet, *Repert*, 33, 92). — A preliminary purification may be effected by dissolving the precipitate in acids, [especially acetic acid (A. Erdmann)], and again precipitating, the colouring matters then remaining undissolved (Pessina). Hydrochloric acid, in quantity not sufficient for complete solution of the precipitate, leaves the greater part of the colouring matter undissolved, and on carefully adding ammonia [or potash (Bischoff)] to a solution in excess of acid, the colouring matter is precipitated first (Rabourdin, *N. J. Pharm.* 39, 408).

Or the precipitate is boiled with solution of sulphate of copper, whereby the cinchona-bases are converted into sulphates, with simultaneous precipitation of a basic copper-salt; the excess of sulphate of copper is then got rid of by means of hydrosulphuric acid, and the alkaloïds are precipitated by ammonia (Klötte-Nortier, *N. Br. Arch.* 86, 165). In this process colouring matter is likewise dissolved (Wittstein). — The alcohol employed for exhausting the precipitate must be decanted cold in the case of quinine, hot in the case of cinchonine (Duflos). Thiboumery (*N. J. Pharm.* 16, 369) employs oil of turpentine or coal-oil, Herring also benzene, for the exhaustion, these substances dissolving quinine and giving it up again to dilute acids. With precipitates free from lime, hot fatty oils may also be used. — Charcoal containing lime occasions a loss of substance in acid solutions (Winckler, *Mag. Pharm.* 19, 258).

Lebourdais (*N. Ann. Chim. Phys.* 24, 65; *Ann. Pharm.* 67, 251; *J. pr. Chem.* 45, 363) boils 1 pound of powdered calisaya bark with water containing sulphuric acid, and filters the decoction through charcoal previously washed with water, whereupon the liquid runs through colourless and tasteless. The washed and dried charcoal boiled with alcohol of 85 p. c., gives up to that liquid the quinine, which is recovered by evaporating the solution. — When an alcoholic extract of the bark is exhausted with water, and the aqueous liquid is filtered, first through paper, and then through animal charcoal purified by hydrochloric acid, the liquid running through is tasteless, and the charcoal gives up quinine and resin to alcohol. The resin may be removed by precipitation with neutral acetate of lead before filtering.

W. Clark (*Lond. Journal of Arts*, Feb. 1864, 94; *Polyt. Notizbl.* 15, 157; *Kopp's Jahresber.* 1860, 362) mixes the extract of the bark, prepared with acidulated water, with not too great an excess of ammonia or carbonate of soda, and boils it with commercial stearic acid, which gradually takes up the alkaloïds and rises with them to the surface of the liquid in the form of a black cake. After cooling, the cake is boiled with water containing sulphuric acid, which takes up the alkaloïds.

The filtered liquid is neutralised with caustic potash, and again filtered from the dark precipitate thereby produced; the sulphate of quinine then crystallises out on cooling.

The residues of cinchona-barks used for pharmaceutical extracts still yield quinine and cinchonine (Peters, *N. Br. Arch.* 46, 284; Schlotfeldt, *N. Br. Arch.* 60, 186; Maillet, *N. J. Pharm.* 14, 352).

*Estimation of Quinine and Cinchonine in Cinchona-barks.* — 1. Ten grammes of the coarsely powdered bark are exhausted with water containing sulphuric acid; to the extract magnesia in excess is added, and the whole is evaporated to dryness over the water-bath. The residue is triturated, the quinine is extracted by ether, and afterwards the cinchonine by alcohol. The colourless extracts contain almost pure alkaloïds; they turn slightly yellow only on evaporation, and leave quinine or cinchonine with a small quantity of inseparable bitter substance (C. Claus, *Russ. Pharm. Zeitschr.* 1, No. 34; *Pharm. Viertelj.* 13, 244). — 2. Forty grammes of the powdered bark, moistened with water containing 2 p. c. of hydrochloric acid, are placed in a percolator, and exhausted with slightly acidulated water, until the liquid flows off free from colour and bitterness, for which purpose 200 to 250 grammes are necessary. The extract is then shaken with 5 or 6 grammes of caustic potash, and 10 to 15 grammes of chloroform, and set aside for half an hour. The chloroform, which has taken up the whole of the quinine, is separated, washed repeatedly with water by decantation, and evaporated over the water-bath. The residue contains the alkaloïds, contaminated with cinchona-red; it is dissolved in dilute hydrochloric acid, filtered, and freed from cinchona-red by the cautious addition of dilute ammonia. After filtering from the red-brown flocks, the addition of more ammonia to the colourless filtrate throws down the pure alkaloïds (Rabourdin, *Compt. rend.* 31, 782; *N. J. Pharm.* 19, 11). The cinchonine [in case it is taken up by the chloroform (Kr.)] and the quinine are then separated by means of ether. A similar process is adopted by Kleist (*Pharm. Viertelj.* 7, 584), and by O. Berg (*Handwörterb*, 2nd ed. 2 [2], 987) and Schacht (*N. Jahrb. Pharm.* 20, 166). — 3. Fifty grammes of the powdered bark are exhausted, first with alcohol of sp. gr. 0·87, and afterwards with dilute hydrochloric acid, for which several days' digestion are necessary. The alcoholic extract is evaporated; the acid extract is added to the residue; and the whole is concentrated and precipitated with phosphomolybdic acid. The precipitate, mixed with hydrate of baryta, is dried and boiled with alcohol; the alcoholic liquid is filtered and evaporated; and the residue is dissolved in dilute sulphuric acid. The acid solution shaken with ammonia and chloroform, gives up to the latter liquid the quinine, which is left on evaporation (De Vrij, *N. Jahrb. Pharm.* 14, 243).

For the separation of quinine, cinchonine, quinidine, and a fourth base, which occurs in Java cinchona-bark (see below), the solution in as small a quantity as possible of strong alcohol is neutralised with hydriodic acid; the hydriodate of quinidine, which separates after 24 hours, in the form of a sandy powder, is removed by filtration; the filtrate is mixed with caustic soda to alkaline reaction; and the cinchonine is allowed to crystallise. On longer standing, cauliflower-like crystals of the fourth alkaloïd also separate, and may be purified by crystallisation from alcohol. The mother-liquor, exactly neutralised with dilute sulphuric acid, and decolorised by animal charcoal, yields nearly colourless sulphate of quinine (De Vrij).

For other methods of testing cinchona barks, see Tilley (*Bull. des scienc. technol.* 1828, 17; abstr. *Schw.* 54, 386), Göbel & Kerst (*Schw.* 54, 384), Tromsdorff (*N. Tr.* 18, 2, 60), Duflos (*Schw.* 62, 310), O. Henry (*J. Pharm,* 16, 754; *Repert.* 37, 120), Marggraf (*Pharm. Zeitschr.* 1850, 81; *Kopp's Jahresber.* 1850, 616), A. Buchner, sen. (*Repert.* (3) 8, 145), Winckler (*Jahrb. pr. Pharm.* 25, 133), O. Henry, jun., (*N. J. Pharm.* 24, 400; abstr. *Pharm. Centr.* 1854, 92), Riegel (*N. Br. Arch.* 70, 162), Faget (*N. J. Pharm.* 37, 13), Glénard & Guillermond (*Compt. rend.* 47, 831; *N. J. Pharm.* 37, 5), Guillermond (*N. J. Pharm.* 41, 40).

Concerning the detection of quinine in the urine, see Robert (*N. J. Pharm.* 4, 197), Bonnewyn (*N. J. Pharm.* 27, 387), Kletzinsky (*N. Repert.* 2, 567; *Pharm. Centr.* 1854, 239), Herapath (*Phil. Mag.* [4] 6, 171; *J. pr. Chem.* 61, 87). A portion only of the quinine administered is found in the urine, the greater part being decomposed in the system (Herapath). See on the contrary, Briquet (*Compt. rend.* 27, 549).

The hydrate of quinine obtained by precipitating a solution of the sulphate by potash or ammonia, may be dehydrated by fusion in a vacuum, or by prolonged heating to 120°.

*Properties.* White, opaque mass, having a crystalline surface and a concentric radiated fracture; fusible to a transparent liquid. When rubbed with a cloth it becomes strongly negatively electric. Permanent in the air, inodorous, very bitter, and antifebrile. Restores the blue colour of reddened litmus paper (Pelletier & Caventou; Dumas). Exerts a left-handed action on polarised light $[\alpha] r = 141.33°$ at 25° (De Vrij & Alluard), $= 121.5°$ at 22.5°, and 129.59° at 16°, weaker, therefore, in warm than in cold solutions. Acids increase the rotatory power, but ammonia reduces it to the original amount (Bouchardat, *N. Ann. Chim. Phys.* 9.213). $[\alpha] j$ in acetic or sulphuric solution $= 287.16°$ at 24° (consequently $[\alpha] r = 220.15°$) (De Vrij & Alluard, *N. J. Pharm.* 46, 192; *Compt. rend.* 59, 201). — Prevents putrefaction (Robin, *Compt. rend.* 32, 650). Not sublimable.

| | | *Fused.* | | Pelletier & Dumas. | Regnault. | Liebig. | Laurent. | Strecker. |
|---|---|---|---|---|---|---|---|---|
| 40 C | | 240 | | 74.07 | 75.02 | 73.38 | 74.09 | 73.41 | 74.05 |
| 2 N | | 28 | | 8.64 | 8.45 | 8.55 | | | |
| 24 H | | 24 | | 7.41 | 6.66 | 7.65 | 7.57 | 7.10 | 7.50 |
| 4 O | | 32 | | 9.88 | 9.87 | 10.42 | | | |
| $C^{40}N^2H^{24}O^4$ | | 324 | | 100.00 | 100.00 | 100.00 | | | |

According to Pelletier & Dumas, $C^{20}NH^{10}O^2$; according to Regnault, $C^{41}N^2H^{25}O^4$; according to Laurent, $C^{38}N^2H^{22}O^4$. The correct formula was deduced from Liebig's analyses, and was doubled by Regnault to that given above. (See p. 201.)

*Decompositions.* 1. In the fire quinine turns brown, burns with flame, evolving an aromatic odour, and leaves a bulky, easily combustible charcoal (Duflos; Pfaff; Merck). No sublimate is obtained thereby (Nesenbeck, *Ann. Pharm.* 6, 319). — When hydrate of quinine is heated for a long time in the air, a portion is sublimed, according to Stratingh, in the form of a yellow powder. — 2. Solutions of quinine-salts turn brown in *sunshine* (Geiger) in a few hours (Pasteur). — 3. They are violently acted on by the *electric current* (Hlasiwetz & Rochleder). — 4. With aqueous *nitrate of potash* sulphate of quinine evolves nitrogen, and is converted into oxyquinine (Schützenberger). — 5. A solution of quinine in strong *nitric acid* becomes coloured on heating (Riegel), without forming picric acid (Liebig). — 6. A solution in oil of vitriol immediately colours *chromate*

*of potash* dark-green, with evolution of gas (Riegel; Eboli). —
7. *Permanganate of potash* acts upon quinine in the cold and more completely at boiling heat, forming carbonate and nitrate of potash, and a peculiar acid (Cloez and Guignet, *Compt. rend.* 47, 710). An aqueous solution containing ½ to 1 per cent. of quinine is not acted on (Menier). —
8. *Peroxide of lead* colours a solution of quinine in sulphuric acid greybrown (Riegel); when employed in the same way as with cinchonine, it produces a blood-red bitter substance, soluble in alcohol and ether, and also without decomposition, in sulphuric and nitric acids, forming solutions of its own colour; it produces also blood-red crystals, which separate from an alcoholic solution on spontaneous evaporation, and dissolve in alcohol and ether with violet, and in acids with red colour; and, at length, as the ultimate product of oxidation, a mixture of acids is obtained (E. Marchand, *N. J. Pharm.* 4, 27). See also *J. Chim. méd.* 20, 363.

9. In contact with *zinc* and dilute *sulphuric acid*, quinine takes up 2 at. water, and is converted into hydroquinine (Schützenberger). —
10. When heated to 240 or 260° with *water* in a sealed tube, it forms chinoline (Reynoso, *Compt. rend.* 34, 795).

11. The colourless solution [yellow according to Guy] of quinine in *oil of vitriol* acquires a yellowish-brown colour when heated (Riegel); *fuming sulphuric acid* colours quinine yellowish-green (Schlienkamp), forming quinine-sulphuric acid (Schützenberger). — Salts of quinine, heated alone, or with sulphuric acid and water, behave in the same manner as salts of cinchonine, save that quinicine is formed instead of cinchonicine (Pasteur). — 11*a*. Anhydrous phosphoric acid, heated with quinine to 140°, produces a brisk evolution of gas, which burns with a pale-yellow flame, and is but slightly soluble in water (Wertheim).

12. Quinine assumes a dirty-yellow colour in vapour of *iodine* (Donné). When triturated with iodine, it behaves in the same way as cinchonine (Thompson). Pelletier's iodoquinine is obtained in the same manner as iodocinchonine, and resembles that body, but contains 69·69 p. c. of quinine and 30·31 of iodine (equal numbers of atoms = 71·7 p. c. quinine, 28·3 iodine). — Quinine is completely precipitated by biniodide of potassium (Wagner). — It is decomposed by aqueous *periodic acid*, with liberation of iodine (Bödeker). — When quinine, or its sulphate, is warmed with an equal quantity of *iodic acid*, an explosive evolution of gas takes place (Brett, *N. J. Pharm.* 27, 116; *N. Repert.* 4, 329).

Quinine, *sulphuric acid*, and *iodine* together yield sulphate of iodoquinine (Herapath). See p. 311.

14. Quinine exposed to a current of dry *chlorine* takes up a large quantity of the gas; according to André, it assumes a carmine-red colour in a few seconds, and becomes soluble in water; but according to Pasteur, it turns greenish, and then gives up to boiling or cold water only a small quantity of a substance having an acid reaction, whilst the remainder behaves like the body formed by the action of chlorine on quinine suspended in water. — Quinine suspended in water is reddened by chlorine (André; Pelletier). A solution of quinine in 400 parts of water acidulated with sulphuric acid, is not coloured or rendered turbid on passing chlorine into it for 10 minutes (Lepage, *J. Pharm.* 26, 140).

A solution of the carmine-red substance in water is rendered green by ammonia, provided it has not been too strongly heated, or the chlorine allowed to act too long. — On passing chlorine for ¾ or 1 hour into a litre of water in which 5 grammes of quinine are suspended, the quinine dissolves completely, and the liquid afterwards becomes turbid from the formation of a white precipitate; after 1½ hour the green colour is no longer produced by ammonia. During the reaction a tear-exciting odour is evolved. The white precipitate turns brownish on drying, and is converted by hot water into a soluble reddish-brown substance. It dissolves with difficulty even in strong acids, but is very easily soluble in alkalis; the solution in alcohol is acid and very bitter. A further quantity of this substance is obtained by partially neutralising the liquid (André, *Ann. Chim. Phys.* 71, 195). The following statements of Pelletier differ from the foregoing: on passing chlorine into quinine suspended in water till solution is effected, the liquid assumes a rose colour, changing to violet, and afterwards to dark-red; on continuing the stream of gas, the liquid becomes paler and deposits a sticky substance, more of which is obtained by neutralising the acid filtrate with ammonia, and evaporating. Sulphate of quinine suspended in water is dissolved by passing a stream of chlorine into it, the liquid passing through yellow and red to green, and afterwards depositing grey flocks, after the removal of which, ammonia throws down only a slight precipitate. If the stream of chlorine be interrupted when the liquid has acquired a red colour, ammonia throws down from the liquid the same sticky precipitate. This precipitate, when freed from acid by boiling water and dried, is friable, brown, and less bitter than quinine; it is deposited from an alcoholic solution, on spontaneous evaporation, in the form of a granular powder, which seems, under the microscope, to consist of microscopic four-sided prisms. It is very slightly soluble in cold, and somewhat more freely in boiling water, and in hot dilute acids, from which it is deposited on cooling; it dissolves also in dilute and in absolute alcohol (Pelletier, *J. Pharm.* 24, 161; *Ann. Pharm.* 29, 54; *J. pr. Chem.* 14, 180).

14*a*. When *chlorine-water* and then *ammonia* are added to a solution of a quinine-salt, a green precipitate is produced, which is dissolved by more ammonia to a fine emerald-green liquid. Exact neutralisation of the liquid colours it sky-blue, changing to violet or fiery-red on further addition of acid; ammonia restores the green colour (André, *J. Pharm.* 22, 132; Meeson, *Phil. Mag.* 1835, 6, 158; Soubeiran & Henry). In this way [especially by employing an ethereal solution (Leers)] mere traces of quinine may be recognised; quinidine, however, exhibits the same reaction.

The green colour is not produced by other alkalis instead of ammonia. It is not produced when the chlorine-water is allowed to act too long, nor with all proportions of chlorine water and ammonia, since with too little chlorine-water ammonia throws down a greenish-white precipitate, and with too much it produces a yellow coloration (Brandes). Reddish-green or brown colours may also be produced (André).

When 200 grains of sulphate of quinine are dissolved in 80 ounces of chlorine-water, and the solution is mixed at once with 10 ounces of ammonia-water, a green precipitate is produced, amounting to about 60 grains, whilst the liquid remains of a deep green colour. The pre-

cipitate is Brandes and Leber's *dalleiochine :* the colouring matter of the solution is not removed by agitation with ether, nor in an unchanged state by other means, but splits up on evaporation into red *rusiochine*, soluble in alcohol, and dark-brown *melanochine*, insoluble in water and alcohol.

*α. Dalleiochine.* — Green granular powder, bitter and inodorous. Contains 58·76 p. c. C., 9·26 N., 6·72 H., 25·26 O., and no chlorine [C$^{40}$N$^3$H$^{27}$O$^{12}$ = 59·2 p. c. C., 10·3 N., 6·6 H. (Kr.)] When heated it behaves like quinine. It is insoluble in cold, and nearly so in boiling water, but easily soluble, with dark red-brown colour, in dilute acids, from which it is precipitated unchanged, of a green colour, by ammonia or carbonate of potash. It dissolves in alcohol, but not in ether.

*β. Rusiochine.* — When the green solution filtered from dalleiochine is evaporated in the air, there remains a dark-brown residue, from which water takes up sal-ammoniac and rusiochine, while melanochine remains undissolved. The solution is evaporated; the sal-ammoniac is removed by repeated solution in alcohol; and the rusiochine is obtained on evaporation in the form of a fine dark-red hygroscopic bitter mass. It contains 43·51 p. c. C., 6·38 N., 9·49 H., and 40·62 O. It dissolves in water and alcohol, and is precipitated from its aqueous solution by ammoniacal lime- and baryta-salts, and by basic acetate of lead and chloride of tin.

*γ. Melanochine.* -- Black-brown, inodorous and tasteless powder, containing 53·71 p. c. C., 7·45 N., 5·87 H., and 32·97 O. Burns, when heated, without melting, evolving ammoniacal vapours. Dissolves in potash and ammonia, but not in water, alcohol, or ether (Brandes & Leber, *N. Br. Arch.* 13, 65; 15, 259). — On quinine-green, see also André (*Ann. Chim. Phys.* 71, 198), Köchlin (*Dingl.* 159, 66; *Chem. Centr.* 1861, 224).

When aqueous sulphate of quinine is mixed with *chlorine* and *ferrocyanide of potassium* in succession, there results a dark-red coloration, passing in a few hours to green, especially on exposure to light (A. Vogel, jun., *Ann. Pharm.* 73, 221). When water is poured upon sulphate of quinine, in such quantity that a large quantity of the salt remains undissolved, a few drops of the solution mixed with an equal quantity of strong chlorine-water free from hydrochloric acid, and finely-powdered ferrocyanide of potassium added a pale, rose-red coloration, passing to very dark-red, is quickly produced : if a dilute solution of ferrocyanide be used, the colour appears on addition of a drop of ammonia-water (Vogel, *Ann. Pharm.* 86, 122 ; *N. Repert.* 2, 289). Instead of ferrocyanide of potassium, the ferricyanide may be employed, and instead of ammonia, lime- or baryta-water, caustic alkalis, or their carbonates, borates, or phosphates (Livonius; Vogel). Kletzinsky (*N. Repert.* 6, 66) mixes a hot saturated solution of ferricyanide of potassium with five times its volume of saturated chlorine-water, adds ammonia to strongly alkaline reaction, and mixes the filtrate with a solution of quinine to which chlorine-water has been previously added, whereby a red or violet colour is produced. — Instead of pulverised ferrocyanide of potassium, a cold saturated aqueous solution of that salt, mixed with an equal quantity of water and $\frac{1}{10}$th its volume of a strong aqueous solution of carbonate of ammonia, may be used (A. Vogel, *N. Repert.* 6, 65).

The red colour changes to green in the light : it is destroyed by mineral acids, and less easily by vegetable acids, but is restored by ammonia (Livonius, *N. Br. Arch.* 77, 6 ; 82, 287). In this way $\frac{1}{10000}$th of quinine may be detected (Flückiger, *Anal. Zeitschr.* 1, 373).

15. Quinine boiled with a very strong solution of *caustic potash*, gives off hydrogen and yields a distillate of chinoline (Gerhardt, *Rev. scient.* 10, 186). When distilled with caustic potash, it behaves like cinchonine (Gerhardt). The decomposition takes place at 170° or 180° ; at a lower temperature formate of potash is also produced (Wertheim, *Wien. Acad. Ber.* 1849, 1, 263). — Quinine heated with caustic soda does not form cyanide of sodium (Rochleder). — 16. With *iodide of methyl*, quinine forms hydriodate of methyl-quinine, which crystallises easily on cooling from solution in boiling water (Stahlschmidt, *Ann. Pharm.* 90, 218). — 17. With *chloride of acetyl* and *chloride of benzoyl*, acetyl-quinine and benzoyl-quinine are obtained, the former substance resembling in every respect the corresponding compound of cinchonine (Schutzenberger).

*Combinations.* — *With Water.* — A. *Hydrate of Quinine.* — Quinine, dehydrated by fusion in a vacuum, takes up 3 to 4 per cent. of water, when immersed therein becoming white and friable.

a. *With 2 at. water.* — When freshly precipitated and washed quinine is spread out and exposed to the air, and frequently moistened, the amorphous precipitate is slowly transformed into crystals, which dissolve in warm alcohol, crystallise again on cooling, and give up their water of crystallisation at 130° (van Heijningen, *Scheik. Onderz.* 5, 319 ; Lieb, *Kopp's Jahresber.* 1849, 374).

|  |  |  | van Heijningen. |  |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ | 324 | 94·74 |  |  |
| 2 HO | 18 | 5·26 | 5·07 |  |
| $C^{40}N^2H^{24}O^4 + 2$ aq. | 342 | 100·00 |  |  |

This hydrate forms van Heijningen's *Gamma-quinine*. It dissolves less easily than quinine in alcohol, and forms a mono-sulphate which differs from the ordinary salt, and loses 4·47 p. c. of water at 130° (2 at. = 4·61 p. c. HO). De Vrij (*N. Jahrb. Pharm.* 14, 268) did not succeed in preparing it.

b. *With 6 at. water.* — Ordinary hydrate of quinine. — Obtained by precipitating aqueous quinine-salts with pure alkalis, washing the precipitate, and drying it in the air. — Loose, white, easily pulverisable mass, melting to a colourless oil at 120° (Duflos), and losing its water at 120—130°, after which it solidifies to a translucent resin on cooling, or when carefully melted in a vacuum, to a crystalline mass.

|  | Air-dried. | | Regnault. at 130°. | Fused. | van Heijningen at 110—130°. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ | 324 | 85·72 |  |  |  |
| 6 HO | 54 | 14·28 | 13·46 | 14·19 | 14·27 |
| $C^{40}N^2H^{24}O^4 + 6$ aq. | 378 | 100·00 |  |  |  |

According to Kiessling (*Pharm. Viertelj.* 8, 339) precipitated and air-dried quinine loses 3·92 p. c. of water at 100° ; it then contains 7·16 p. c. of nitrogen, and

150° is, therefore, the hydrate with 6 at. water ( calc. 7·41 p. c. N.).   At 100° to it further loses 1·92 p. c. in weight, probably partly volatilised quinine, and melts at about 196°. — According to Hanamann (*Pharm. Viertelj.* 12, 526), when a perfectly cold solution of sulphate of quinine in water containing sulphuric acid is precipitated by ammonia, and the precipitate is washed and dried in the air, a very light powder is obtained, melting to a glassy colourless mass, and losing 20 p. c. of water at 120°. If the solution be precipitated hot, the precipitate runs together and becomes glassy, and on drying forms a horny mass, losing 8·75 p. c. of water at 120°.   See also Wittstein (*Pharm. Viertelj.* 12, 258). — According to Magouty (*J. Chim. méd.* 16, 244) quinine becomes anhydrous at 60°.   According to Duflos, the hydrate thrown down by alkalis loses 4½ p. c. of water on melting at 120°.

*Crystallised Hydrate of Quinine* separates from a solution in alcohol of 40° to 42° B. on evaporation in dry cold air, in tufts of silky needles, whereas on evaporating a solution in alcohol of 38° B., or on mixing the alcoholic solution with water, an amorphous hydrate is obtained, drying up to a transparent resin, which melts at 90° (Pelletier Caventou; Dumas).   From absolute alcohol, van Heijningen obtained a resin with few crystals.   A hot aqueous solution containing a little ammonia, yields fine needles on prolonged standing (Liebig; van Heijningen).   Duflos and Magouty also obtained crystals, the former from alcohol, the latter from water.   See also the behaviour of the salts towards carbonate of ammonia.

Quinine dissolves in 364 parts of cold *water* (Duflos); in 480 parts of water at 18·75° (Abl); in 200 parts (Pelletier & Caventou), 267 parts (Duflos), of boiling water.   It dissolves easily in water containing sal-ammoniac (Calloud).

Quinine does not combine with *sulphur* (Pelletier). — A solution in 30 to 35 parts of *bisulphide of carbon* solidifies in a day or two to a transparent, very firm jelly (Lepage, *N. Br. Arch.* 97, 240).

Quinine is not insoluble in aqueous *alkalis* and in *ammonia*, especially when freshly precipitated.   According to Duflos, however, aqueous quinine is precipitated by pure alkalis and by their carbonates and bicarbonates, so that the presence of acids probably influences its solubility. — It dissolves in 2,146 parts of lime-water (Calvert).

*With Acids.* — Quinine neutralises acids completely, forming *mono-* and *bi-acid* salts.   The salts are, for the most part, more easily crystallisable and less soluble in water than the salts of cinchonine.   They have a strong bitter taste, and frequently exhibit a pearly or silky lustre.   They are precipitated by alkalis and their carbonates, by the hydrates of lime and magnesia, and by ammonia and carbonate of ammonia, hydrate of quinine being thrown down in white flocks. The precipitate produced by potash, ammonia, or carbonate of potash is pulverulent, and not crystalline nor soluble, to any great extent, even in excess of the precipitant; the sulphate alone yields a precipitate easily soluble in excess of ammonia (v. Planta).   The hydrate precipitated from a cold aqueous solution of the sulphate dissolves in ammonia far more easily than the other cinchona bases;  the hydrate thrown down in clotty masses from strong solutions of the salts is difficultly soluble (Kerner, *Anal. Zeitschr.* 1, 162).   Carbonate of ammonia added to sulphate of quinine throws down crystalline needles after some hours; from the hydrochlorate and acetate it precipitates a heavy powder, which dissolves in excess of the precipitant, and is deposited again in needles on standing for an hour (v. Planta). Quinine expels ammonia from its salts when boiled therewith (Ma-

gouty). — Bicarbonate of soda immediately throws down from strong solutions of quinine-salts a white pulverulent precipitate (v. Planta), and from dilute solutions, after some time, tufts of needles (Riegel); but solutions of the salts in 300 parts or more of water are not pre-cipitated by it, or are precipitated only after several hours, after the addi-tion of tartaric acid (Oppermann ; Riegel). Pentasulphide of potassium throws down from boiling solutions of quinine-salts a red turpen-tine-like mass (Palm). Cyanide of potassium colours the salts carmine-red (Schwabe). Lime-water added in excess to quinine-salts dis-solves the precipitate formed at first (Riegel; Calvert). Solutions of quinine-salts containing excess of acid are highly fluorescent.

*Carbonate of Quinine.* — The precipitate thrown down by alkaline carbonates from quinine-salts retains a little of the precipitant, but is free from carbonate of quinine, since it does not evolve carbonic acid when heated (Langlois, *Ann. Pharm.* 32, 126). When the quinine precipitated from 10 grammes of the sulphate by ammonia is suspended in water, and carbonic acid is passed into the solution for an hour, the quinine dissolves completely to an alkaline liquid, from which crystals of carbonate of quinine are deposited on exposure to the air for twenty-four hours. By spontaneous evaporation of the mother-liquor, quinine is obtained free from carbonic acid. — Translucent needles, having an alkaline reaction, efflorescing rapidly in the air, and decomposing at 110°, with liberation of carbonic acid ; they are soluble in alcohol, but insoluble in ether (Langlois, *N. Ann. Chim. Phys.* 41, 89 ; *Ann. Pharm.* 88, 320).

|  | | Crystals. | | | | Langlois. |
|---|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ | | 324 | ........ | 80·19 | ........ | 80·45 |
| 2 $CO^2$ | | 44 | ........ | 10·89 | ........ | 10·58 |
| 4 HO | | 36 | ........ | 8·92 | ........ | 8·97 |
| $C^{40}N^2H^{24}O^4,2HO,2CO^2$ + 2 aq. | .... | 404 | ........ | 100·00 | ........ | 100·00 |

*Borate of Quinine.* — A solution of quinine in hot aqueous boracic acid yields crystalline granules on cooling; by spontaneous evapora-tion with an excess of boracic acid, a varnish is obtained (Serullas, *Ann. Chim. Phys.* 45, 282).

*Hypophosphite of Quinine.* — 100 parts of sulphate of quinine are heated to 94° with 6,000 parts of water and 38·7 parts of hypophos-phorous acid ; a quantity of hypophosphite of baryta barely sufficient for the complete decomposition of the sulphate is then added, and the liquid is filtered and left to crystallise. The mother-liquor and wash-water yield colourless crystals only when cautiously evaporated. — Light, very loose mass, having a pure bitter taste. Melts and turns brown at 150°, with loss of water. — Dissolves in 60 parts of water at 15·5°, and more easily in boiling water (L. Smith, *Amer. J. Pharm.* 31, 285 and 32, 410 ; *Zeitschr. Ch. Pharm.* 5, 159 ; *J. pr. Chem.* 83, 127).

|  | | | | | | L. Smith. |
|---|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ | | 324 | ........ | 83·09 | ........ | 83·00 |
| PO | | 39 | ........ | 10·00 | ........ | 10·09 |
| 3 HO | | 27 | ........ | 6·91 | ........ | *a.* 2·30 <br> *b.* 4·60 |
| $C^{40}N^2H^{24}O^4,PH^3O^4$ | .... | 390 | ........ | 100·00 | ........ | 99·99 |

T 2

S mith gives the formula $C^{40}N^2H^{24}O^4,PHO^2 + 2$ aq., and distinguishes *a* as hydrate-water, *b* as water of crystallisation. The formula of the salt, therefore, remains doubtful (Kr.).

*Pyrophosphate of Quinine.* — Obtained by precipitating hydrochlorate of quinine with ignited phosphate of soda (Winckler, *Repert.* 41, 418).

*Phosphate of Quinine.* Phosphate of soda throws down from cold aqueous solutions of hydrochlorate or acetate (but not from sulphate) of quinine, a dense precipitate, which soon turns crystalline (v. Planta). A hot solution of sulphate or hydrochlorate of quinine, mixed with a slight excess of phosphate of soda, deposits on cooling a white crystalline mass, very slightly soluble in water. After drying in the air it forms a loose mass, made up of microscopic four-sided prisms. Contains 12·38 p. c. of phosphoric acid, and 4·56 p. c. of water, which is expelled at 100° (Winckler, *Repert.* 34, 260; 41, 418; 99, 20). Dissolves very easily in hydrochloric acid (v. Planta).

The quickly formed solution of quinine in warm aqueous phosphoric acid solidifies on cooling to a mass of needles. Dilute solutions yield radiated groups of delicate, silky needles, which unite into a mass on drying. Neutral. Loses 7·57 to 7·87 p. c. of water at 127°; other crystals, of similar properties in other respects, lost 15·3 p. c. of water on warming (10 at. = 7·1; 24 at. = 15·6 p. c. HO) (Anderson, *Ann. Pharm.* 66, 59).

|  |  | *at* 100°. |  |  |  | Anderson. |
|---|---|---|---|---|---|---|
| 120 C | .............................. | 720 | ........ | 61·65 | ..... ... | 61·85 |
| 6 N | .............................. | 84 | ........ | 7·19 |  |  |
| 78 H | .............................. | 78 | ........ | 6·69 | ........ | 6·81 |
| 18 O | .............................. | 144 | ........ | 12·32 |  |  |
| 2 PO⁵ | ............................. | 142 | ........ | 12·15 |  |  |
| 3C⁴⁰N²H²⁴O⁴,2PO⁵,6HO.... | | 1168 | ........ | 100·00 |  |  |

Anderson supposes the salt to contain 12 at. water of crystallisation, corresponding to 8·4 p. c. The correctness of his formula is doubtful. See *Kopp's Jahresber.* 1847 and 1848, 616; Gerhardt (*N. J. Pharm.* 14, 52).

*Hyposulphite of Quinine.* — Formed in a mixture of quinine, alcohol, and hydrosulphate of ammonia, on standing in the air (How). Hyposulphite of soda immediately throws down from a moderately concentrated aqueous solution of hydrochlorate of quinine, a dazzling white precipitate, nearly insoluble in cold water, dull and crystalline after drying (Winckler, *Jahrb. pr. Pharm.* 15, 286). A solution of the washed precipitate in hot alcohol yields, on cooling, fine semi-transparent needles, breaking up at 100°, from loss of water of crystallisation [4·57 to 4·67 p. c. = 2 at. (How)], into a powder, which is very electric when warm (Wetherill, *Ann. Pharm.* 66, 150), — Dissolves in 300 parts of cold, and easily in hot water (H. How, *N. Edin. Phil. J.* new ser. 1, 47; *Pharm. Centr.* 1855, 93).

|  |  | *at* 100°. |  |  |  | Wetherill. |  | H. How. |
|---|---|---|---|---|---|---|---|---|
| 40 C | ........................... | 240 | ........ | 62·99 | ........ | 61·35 | ........ | 62·82 |
| 2 N | ........................... | 28 | ........ | 7·36 | ........ | 8·30 |  |  |
| 25 H | ........................... | 25 | ........ | 6·56 | ........ | 6·72 | ........ | 6·76 |
| 7 O | ........................... | 56 | ........ | 14·69 | ........ | 15·14 |  |  |
| 2 S | ........................... | 32 | ........ | 8·40 | ........ | 8·49 | ........ | 8·30 |
| C⁴⁰N²H²⁴O⁴,HO,S²O² .... | | 381 | ........ | 100·00 | ........ | 100·00 |  |  |

*Sulphite of Quinine.* Dry quinine absorbs sulphurous acid gas, with considerable evolution of heat, and forms an anhydrous salt (Liebig & Pelouze, *Ann. Pharm.* 19, 256).

*Hyposulphate of Quinine.* When a hot saturated solution of sulphate of quinine is precipitated by hyposulphate of baryta, the filtered liquid deposits crystals on cooling (Herren, *Pogg.* 7, 193).

*Sulphate of Quinine.* — A. *Mono-acid. Basic sulphate* (Preparation p. 264). — Delicate, silky, slightly flexible needles, or longish laminæ (Pelletier & Caventou). Diclinic. Rectangular prisms, obliquely truncated (similar to fig. 92), distinctly cleavable parallel to $i$ and $t$, less distinctly parallel to $m$. Angle $m : t = 90°$; $i : t = 96° \; 30'$ ; $i : m = 95° \; 50'$. Frequently also hemitropic, or rather quadruple crystals (Brooke, *Phil. Ann.* 6, 375). Light and loose, like magnesia. Tastes very bitter.—Exerts a left-handed action on polarised light; $[\alpha]j$ for anhydrous sulphate $= 255\cdot6°$; for sulphate with 15·72 p. c. water $= 210\cdot87°$ (De Vrij & Alluard, *Compt. rend.* 59, 201). See also Bouchardat (*N. Ann. Chim. Phys.* 9, 213).

At a temperature of 160°, it becomes luminous when rubbed (Calloud), exhibiting a pale-green light, brighter than that of the cinchonine-salt (Stratingh), and becomes positively electric (Pelletier & Dumas). A few ounces of the salt warmed in a silver basin are highly phosphorescent on cooling (Landerer, *N. Repert.* 7, 275). — Neutral towards vegetable colours (Pelletier & Caventou ; Baup); slightly alkaline according to Robiquet, and Delondre & Henry. — Turns brown in sunshine, both in the dry and in the moist state (Leverköhn, *Kastn. Arch.* 17, 128); when exposed to the sun for 7 weeks, it assumes a cinchona-brown colour (*Br. Arch.* 28, 235).

The sulphate dried in the air at 8° to 15°, or over oil of vitriol diluted with 3·2 to 3·5 its volume of water, has the composition $2C^{40}N^2H^{24}O^4,2(HO,SO^3)+15$ aq. ; the moist salt loses its excess of water when placed over acid of this strength, whilst the air-dried salt does not alter in weight. When heated to 110° to 120°, it loses the whole of its water of crystallisation, but rapidly absorbs 4·87 to 5·1 p. c. again on exposure to moist air (4 at. = 4·82 p. c.) (Jobst & Hesse) ; the same quantity of water is retained by the salt dried over oil of vitriol [or in dry air (Baup)]. A solution of 1 part of the air-dried salt in 40 parts or more of alcohol of sp. gr. 0·852, deposits on evaporation white needles containing 4 at. of water (Jobst & Hesse).

Millon & Comaille (*N. J. Pharm.* 42, 377; *Kopp's Jahresber.* 1862, 368), also found the sulphate dried over oil of vitriol at 15°, to contain 4·6 to 4·8 p. c. of water, whilst the air-dried salt did not lose weight over oil of vitriol with 18 at. of water at 15°. The sulphate dried over oil of vitriol at 30° retains 0·93 p. c. ; that dried over oil of vitriol with 4 at. of water at 15°, 6 p. c. of water. The salt rendered anhydrous by drying at 120° takes up 39 p. c. of water on exposure to very moist air for 5 to 8 days, at a temperature of 15° to 18°.

|  |  | Dried. |  |  | Regnault. | Strecker. |
|---|---|---|---|---|---|---|
| 40 C | ............... | 240 | ........ | 64·36 | ........ 64·06 |  |
| 2 N | ............... | 28 | ........ | 7·51 |  |  |
| 25 H | ............... | 25 | ........ | 6·70 | ........ 6·98 |  |
| 5 O | ............... | 40 | ........ | 10·71 |  |  |
| SO$^3$ | ............... | 40 | ........ | 10·72 | ........ | ........ 10·75 |
| $C^{40}N^2H^{24}O^4,HO,SO^3$.... | 373 | ........ | 100·00 |  |  |  |

|  | Over oil of vitriol. | | Baup. Effloresced. | Strecker. Air-dried. a. | Jobst & Hesse. b. |
|---|---|---|---|---|---|
| 2 C⁴⁰N²H²⁴O⁴ | 648 | 82·86 | | | |
| 2 SO³ | 80 | 10·23 | 9·57 | | |
| 2 HO | 18 | 2·31 | | | |
| 4 aq. | 36 | 4·60 | 4·31 | 4·6 | 4·64 .... 4·66 |

2C⁴⁰N²H²⁴O⁴,2(HO,SO³) + 4 aq..... 782 .... 100·00

a was dried over oil of vitriol, b crystallised from alcohol.

|  | Crystallised. | | Baup. | Delondre & Henry. | Jobst & Hesse mean. |
|---|---|---|---|---|---|
| 2 C⁴⁰N²H²⁴O⁴ | 648 | 73·55 | | | |
| 2 SO³ | 80 | 9·08 | 8·47 | 9·3 | 9·11 |
| 2 HO | 18 | 2·04 | | | |
| 4 aq. | 36 | 4·09 | | | |
| 11 aq. | 99 | 11·24 | 11·75 | 15·2 | 15·37 |

2C⁴⁰N²H²⁴O⁴,2(HO,SO³) + 15 aq. .... 881 .... 100·00

Regnault's salt lost 13·99 p. c. of water in a current of air at 120°, and no more at 140°.

Commercial sulphate of quinine contains quantities of water varying between 5·1 and 13·3 p. c. (Millon & Comaille). It usually appears half-effloresced, but still contains 15·6 p. c. of water (Guibourt). Ch. Link (*Proc. Amer. Assoc.* 1849, 275 ; *Kopp's Jahresber.* 1850, 419) found in the commercial sulphate 9·8 p. c. SO³, and 8·4 p. c. of water, which was expelled at 130°.

Sulphate of quinine does not decompose at 155° (Millon & Comaille). It melts more easily than sulphate of cinchonine to a waxy liquid, which assumes a fine red colour when more strongly heated (Pelletier & Caventou), and evolves purple-red vapours, which condense in the cool part of the tube. This red substance dissolves in water with fine red colour, and is not precipitated by acetate of lead or baryta, but is decolorised by potash or ammonia (Kastner, *Kastn. Archiv.* 20, 418). See also Jonas (*N. Br. Arch.* 17, 287), Wigand (*N. Br. Arch.* 115, 230). Burns at last with an empyreumatic odour, leaving at first a shining, and afterwards also a combustible charcoal.

The anhydrous salt dissolves in 793 parts of water at 6°, and in 788 parts at 9·5° (Jobst & Hesse). One part of the salt (crystallised or dry ?) dissolves in 265 parts of cold, and in 24 parts of boiling water (Bussy & Guibourt) ; in 335 parts cold, and 33·5 parts boiling (Howard) ; in 720° parts at 18·75° (Abl) ; in 740 parts at 13°, and in 30 parts at 100° (Baup) : in 740 parts at 10° (van Heijningen ; Cap & Garot). The commercial salt dissolves in 738 to 770 parts of water at 12° to 15°, in not quite constant proportions (Kerner). Dissolves very sparingly in a cold saturated solution of Glauber's salt, and scarcely at all in Rochelle salt, so that the solution is scarcely clouded by ammonia, or coloured by chlorine-water and ammonia (Mann). The solubility of sulphate of quinine in water is reduced by sulphate of soda and sulphate of magnesia, but increased by sal-ammoniac, saltpetre, and chlorate of potash (Calloud, *Pharm. Journ.*, June 1860, 609 ; *N. Vogel. Notiz.* 13, 276).

One part of anhydrous sulphate of quinine dissolves in 100 to 115 parts of alcohol of sp. gr. 0·852; the strength of the alcohol, however, is altered by the salt dissolved in it (Jobst & Hesse, *Ann. Pharm.* 119, 361; abstr. *J. pr. Chem.* 85, 309; *N. Ann. Chim. Phys.* 64, 364). One part of the salt (crystallised or dry?) dissolves in 60 parts of cold alcohol of sp. gr. 0·85 (Baup); in 60 parts of cold alcohol of 21° (Delondre & Henry); in 40 parts of alcohol (Cap & Garot); in 7·5 parts of boiling alcohol of 90 p. c. (Bussy & Guibourt), from which it is deposited almost entirely on cooling. — Sulphate of quinine dissolves in 40 parts of glycerin, but not in fatty oils (Cap & Garot; Attfield). It dissolves abundantly in creosote at 20°, and slowly in cold picamar (Reichenbach). It is insoluble in chloroform (Schlimpert).

*Impurities and Adulterations of Sulphate of Quinine.* — Sulphate of quinine may be intentionally adulterated, either with inorganic substances (such as sulphate or carbonate of lime or magnesia), the presence of which is detected on heating, or with organic substances. Of the latter class of bodies, starch-powder and stearin are recognised by their insolubility in acidulated water, and gum by its insolubility in alcohol; salicin, phlorizin, and cane-sugar assume a red or brown colour with oil of vitriol; the other varieties of sugar, as well as other substances soluble in water, remain in solution on boiling the sulphate with baryta-water, passing carbonic acid into the liquid, and filtering, and may be recognised on evaporating the solution. The pure sulphate thus treated leaves only a slight residue, corresponding to the solubility of quinine in water.

On the adulteration of sulphate of quinine, see Winckler (*Repert.* 97, 403; *Jahrb. pr. Pharm.* 15, 165), Stresemann (*N. Br. Arch.* 52, 151), Sckeyde (*N. Br. Arch.* 56, 171), Legrip (*J. Chim. méd.* 27, 49); with salicin: Peltier (*N. J. Pharm.* 7, 135), Bouxlier (*N. Br. Arch.* 106, 322); with mannite: J. Kral (*Anal. Zeitschr.* 2, 405).

Since cinchonine and quinidine (or cinchonidine) exist together with quinine in cinchona-barks, the sulphates of those bases may occur as impurities in sulphate of quinine: they may be recognised by the following *quinine-test* of Liebig:—10 grains of the sulphate to be tested are warmed with 10 drops of dilute sulphuric acid and 15 drops of water in a test-tube; the solution is cooled; 60 drops of commercial ether and 20 drops of ammonia-water are added; and the whole is shaken and the tube stopped. If the quinine was free from cinchonine and did not contain more than 10 per cent. of quinidine, the whole remains in solution; but if cinchonidine was present, it is deposited as a white pulverulent layer between the ether and the water, as is also the case with quinidine when present in large quantity. Smaller portions of quinidine crystallise from the ether on standing for a short time, and still smaller quantities when ether saturated with quinidine is employed in the first instance. As it sometimes happens that the upper ethereal layer solidifies to a jelly, even with pure sulphate of quinine, it is more convenient to employ ether containing alcohol, or to take a somewhat larger proportion of ether than is directed above. See Merck, Zimmer & Howard (*Jahrb. pr. Pharm*, 24, 209; *Pharm. Journ.* 11, 393; *Pharm. Viertelj.* 1, 437), Wollweber (*N. Br. Arch.* 63, 6), Roger (*N. J. Pharm.* 41, 204; *Pharm. Viertelj.* 11, 398), Bergot (*Zeitschr. Ch. Pharm.* 5, 123), Demeyer (*J. Chim. méd.* 1862, 460; *Pharm. Viertelj.* 12, 256), Kerner (*Anal. Zeitschr.* 1, 150), Jandous (*Apoth. Ver. Zeit.* 1863, 254). Guibourt evaporates the ammonia before adding the ether (*N. J. Pharm.* 21, 47). — Instead

of ether, Riegel (*Jahrb. pr. Pharm.* 25, 340) employs 100 drops of chloroform, whereby the quinidine also is dissolved. To separate this last substance, he dissolves 10 grains of the sulphate in water, with addition of tartaric acid, and adds bicarbonate of soda to the solution. The resulting precipitate consists of cinchonine and quinidine, whilst quinine remains in solution. The cinchonine and quinidine may then be separated by chloroform. — O. Henry (*N. J. Pharm.* 13, 107; *J. Chim. méd.* 24, 258) likewise separates quinine and cinchonine by means of ether or cold alcohol, but first removes the greater part of the quinine by converting it into acetate (by precipitating with caustic soda and dissolving the precipitate in acetic acid) and crystallising out as far as possible. — Delondre & O. Henry (*N. J. Pharm.* 21, 281) triturate 10 grammes of the sulphate and 4 grammes of acetate of baryta with 60 grammes of water and a little acetic acid, separate the crystals which form after a few minutes, and dilute the filtrate with twice its volume of alcohol of 36°. After adding a little sulphuric acid and again filtering, the liquid is boiled with excess of ammonia, and after standing for 24 hours, the cinchonine crystallises in needles. The cinchonine may also be obtained in crystals by dissolving 5 grammes of the sulphate in 120 grammes of warm acidulated alcohol, boiling the solution with excess of ammonia, and setting it aside for 24 hours.

See further: Calvert's method (*N. J. Pharm.* 2, 393, and 13, 341), O. Henry (*N. J. Pharm.* 16, 327), J. Barry (*Repert.* 92, 65; *Pharm. Journ.* 5, 113), Kerner (*loc. cit.*), C. Mann (*Pharm. Viertelj.* 13, 245), Stoddart (*Pharm. Journ.* 6, 241; *Pharm. Viertelj.* 14, 395).

B. *Bi-acid.* — Mono-acid sulphate of quinine dissolves very easily in water containing sulphuric acid. The solution is colourless or pale-yellow by transmitted light, but exhibits blue fluorescence by reflected light (Raupp, *Repert.* 39, 465). It is one of the most highly fluorescent bodies (S. Niepce de Saint-Victor, *J. pr. Chem.* 74, 237 and 241). A solution containing $\frac{1}{100000}$th or less exhibits the fluorescence when a cone of light from a lens is made to fall upon the liquid (Flückiger, *Schweiz. Pharm. Zeitschr.* 7, 22; *Anal. Zeitschr.* 1, 373). — Rectangular prisms, having a bitter, not acid, taste, and reddening litmus (Robiquet). On rapidly cooling the aqueous solution, it forms slender needles; by slow evaporation large transparent prisms (Baup). Rhombic prism $y$ (fig. 53) having its obtuse edges truncated by $a$; a horizontal prism $u$ rests on the acute edges, and the prism $i$ on $p$; further the base $t$ and a face $k$ between $i$ and $t$. Angle $y:y$ (right and left) = 145° 5'; $y:p$ = 107° 27'; $t:i$ = 127° 42'; $t:k$ about = 157°; $t:u$ = 130° 39' 43". The crystals have a tabular form from predominance of $t$; cleavable parallel to $p$ (Hahn, *N. Br. Arch.* 99, 148). — By digestion with water and carbonate of lime, the salt is converted into A. Melts in its water of crystallisation at 100°. Dissolves in 11 parts of water at 13°, and in 8 parts at 22°; and in dilute or absolute alcohol, much more freely in the hot liquids than in the cold. From a solution in absolute alcohol it is deposited in crystals which immediately fall to powder on exposure to the air (Baup).

*Dry.*

| | | | |
|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ | 324 | | 76·78 |
| 2 $SO^3$ | 80 | | 18·96 |
| 2 HO | 18 | | 4·26 |
| $C^{40}N^2H^{24}O^4,2(HO,SO^3)$ | 422 | | 100·00 |

| | Crystals. | | | | Baup. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4,2HO$ .............................. | 342 | ........ | 61·43 | | |
| 2 $SO^3$ .............................................. | 80 | ........ | 14·36 | ........ | 13·70 |
| 15 HO .................................................. | 135 | ........ | 24·21 | ........ | 24·36 |
| $C^{40}N^2H^{24}O^4,2(HO,SO^3)$ + 15 aq. .... | 557 | ........ | 100·00 | | |

Baup found 18·18 p. c. $SO^3$ in the dry salt.

*Iodate of Quinine.* — Formed, together with hydriodate of quinine, on warming iodine with quinine and water (Pelletier & Caventou). See decompositions.

A. *Mono-acid?* — Obtained from aqueous iodic acid and quinine. Crystallises, on evaporating and cooling the solution, in silky crystals like the sulphate. Decomposes when quickly heated, leaving charcoal (Serullas, *Ann. Chim. Phys.* 45, 282). See also p. 270. Less soluble in water than iodate of cinchonine (Pelletier).

B. *Bi-acid?* — Aqueous iodic acid throws down from chlorate or acid sulphate of quinine an acid iodate, a further quantity of which is obtained on adding alcohol to the solution (Serullas).

*Periodate of Quinine.* — Freshly precipitated quinine neutralises aqueous periodic acid but incompletely in the cold, and on warming the liquid, iodic acid is formed. When the acid solution is evaporated over oil of vitriol, it becomes covered with oily drops, which are converted into crystals as the evaporation proceeds. The periodic acid contained in the crystals is reduced on keeping for a short time, the crystals acquiring a yellow colour. — On neutralising the alcoholic solution, and evaporating at 30° to 40°, roundish masses of needles are obtained. They dissolve easily in water containing nitric acid, but with difficulty in pure water, and after drying at 40° retain 18 at., and at 100° 12 at. of water (Langlois, *N. Ann. Chim. Phys.* 34, 274).

| | | | | | Langlois. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ ...................... | 324 | ........ | 49·85 | | |
| $IO^7$ ........................................ | 164 | ........ | 25·23 | ........ | 25·36 |
| 18 HO ...................................... | 162 | ........ | 24·92 | | |
| $C^{40}N^2H^{24}O^4,IO^7,18HO$ .... | 650 | ........ | 100·00 | | |

| | at 100°. | | | | Langlois. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ ...................... | 324 | ........ | 54·36 | | |
| $IO^7$ ........................................ | 164 | ........ | 27·52 | ........ | 27·60 |
| 12 HO ...................................... | 108 | ........ | 18·12 | | |
| $C^{40}N^2H^{24}O^4,IO^7,12HO$ .... | 596 | ........ | 100·00 | | |

Langlois assumes the existence of 22 and 18 at. of water, but he determined only the periodic acid.

*Hydriodate of Quinine.* — Obtained by direct union of the acid and base, or by double decomposition, in nodular groups of delicate crystals (Pelletier). Lemon-yellow prisms (Herapath). A solution of sulphate of quinine in boiling water, mixed with an equal number of atoms of iodide of potassium, yields crystals of sulphate of quinine only on cooling; but when 240 parts of hydrochlorate of quinine are mixed with 460 parts of iodide of potassium, in hot aqueous solution, a colourless turpentine-

like mass is deposited as the liquid cools (Winckler).   Iodide of potassium throws down from acetate or hydrochlorate of quinine, a heavy white powder, which runs into drops (v. Planta). — Melts to a resin over the water-bath.   Dissolves in water more freely than the sulphate ; in nearly all proportions in alcohol, and in ether (Winckler, *Jahrb. pr. Pharm.* 20, 321).

|  |  |  |  |  | Winckler. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{25}O^4$............ | 325 | ........ | 71·91 |  |  |
| I ............................ | 127 | ........ | 28·09 | ........ | 28·42 |
| $C^{40}N^2H^{24}O^4,HI$ .... | 452 | ........ | 100·00 |  |  |

By mixing bi-sulphate of quinine with solution of iodide of potassium, Righini (*J. Chim. méd.* 13, 116) obtained a red powder, containing, according to his analysis, 50 p. c. of quinine, 30 of hydriodic acid, and 20 of iodine, being a mixture of hydriodate of quinine and iodo-quinine. — According to Reignier (*J. Chim. méd.* 13, 119), on dissolving this precipitate in alcohol, and evaporating the solution, transparent 4-sided prisms are obtained, which turn dull and brown-red in the air.

*Chlorate of Quinine.* — Formed by dissolving quinine in warm aqueous chloric acid.   Tufts of delicate needles, melting to a colourless liquid, which solidifies to a transparent varnish.   Explodes when strongly heated (Serullas, *Ann. Chem. Phys.* 45, 279).

*Perchlorate of Quinine.* — When sulphate of quinine is precipitated by perchlorate of baryta, and the filtrate is evaporated, yellowish oily drops are deposited, which redissolve on gently warming the liquid, and afterwards separate in crystals on cooling.   By concentration the mother-liquor yields a further quantity of oil, which solidifies in contact with a crystal. — Striated prisms, exhibiting a faint dichroïsm of blue and yellow (Bödeker).   The crystals belong to the right prismatic system, being truncated rhombic octahedrons, cleavable parallel to the end-face.   Inclination of the octahedral faces, basal = 149° 46′ ; macrodiagonal = 80° 30′ ; brachydiagonal = 107° 32′ (Dauber, *Ann. Pharm.* 71, 65).   The crystal melts at 45°, and likewise at a moderate temperature over oil of vitriol, to a clear brittle mass (? Kr.) which loses 14·3 p. c. of water at 110°, puffs up strongly at 150°, and solidifies again at 160°, having then lost 18·63 p. c. of water.   On further heating, a violent explosion occurs, accompanied by flame. — Aqueous solutions of a certain strength yield highly lustrous, dichroïtic, rhombic tables, which melt to an oil under water, but fuse only at 210° when heated alone, losing 6·5 p. c. of water (4 at. = 6·4 p. c. HO) (Bödeker).

| *Crystals.* |  |  |  |  | Bödeker. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4,2HO$ ........................ | 342 | ........ | 52·53 | ........ | 50·63 |
| 2 ClO⁷ ........................................ | 183 | ........ | 28·11 | ........ | 28·21 |
| 14 HO ........................................ | 126 | ........ | 19·36 | ........ | 18·63 |
| $C^{40}N^2H^{24}O^4,2ClHO^8 + 14HO$ .... | 651 | ........ | 100·00 | ........ | 97·47 |

*Hydrochlorate of Quinine.* — A.  *Mono-acid.*  A solution of quinine in slight excess of hydrochloric acid deposits long silky needles which lose 7·05 p. c. of water in a current of air at 140° (3 at. = 6·96 p. c. HO) (Regnault).   Winckler (*Repert.* 34, 266) takes 1 part of quinine, 1 part of hydrochloric acid, and 4 parts of water, or, since in this way it sometimes happens that crystals are not obtained, Winckler (and

Leverköhn) decompose 100 parts of sulphate of quinine with 25 parts of crystallised chloride of barium, and evaporate the filtrate at a gentle heat (*Repert.* 32, 215). Radiated groups of white, pearly needles (Winckler). Dissolves in water more easily than sulphate of quinine, less easily than hydrochlorate of cinchonine (Pelletier and Caventou); in 24 parts of water at 18·75° (Abl.) — Dissolves in 9 parts of chloroform at 17·5° (Schlimpert) (? Kr.), and slowly in cold picamar (Reichenbach).

| | | at 130°. | | | | Regnault. mean. |
|---|---|---|---|---|---|---|
| 40 | C | 240 | ..... ... | 66·57 | ........ | 66·23 |
| 2 | N | 28 | ........ | 7·77 | ........ | 8·02 |
| 25 | H | 25 | ........ | 6·93 | ... .... | 7·15 |
| 4 | O | 32 | ........ | 8·87 | ........ | 9·32 |
| | Cl | 35·5 | ........ | 9·86 | ........ | 9·28 |
| $C^{40}N^2H^{24}O^4,HCl$ | .... | 360·5 | ........ | 100·00 | ........ | 100·00 |

The crystals contain 8·75 p. c. of water, and 8·82 of hydrochloric acid (Winckler); 6·62 of hydrochloric acid (Pelletier and Caventou).

B. *Bi-acid.* — Quinine absorbs a large quantity of hydrochloric acid gas [24·1 p. c. (Liebig), 22·86 p. c. (van Heijningen) 2 at. = 21·91 ȷ c.], but gives up portions of it continuously in dry air, ceasing to do so only at very high temperatures. Quinine saturated with hydrochloric acid contains, at 145°, 19·31 p. c., at 160° in a current of hydrochloric acid gas, 18·77 p. c. of hydrochloric acid (2 at. = 17·97 p. c. HCl); at a few degrees above 160° it turns yellow. From the highly acid aqueous solution an amorphous gum is obtained (Regnault; van Heijningen).

*Hydrofluate of Quinine.* — A solution of freshly precipitated quinine in aqueous hydrofluoric acid is transformed, when evaporated nearly to dryness, into a crystalline mass of concentrically arranged needles, which deliquesce rapidly in the air and dissolve very readily in alcohol. (Elderhorst, *Ann. Pharm.* 74, 79). Quinine and hydrofluoric or hydrofluosilicic acid (whereby silicic acid is thrown down) yield thin white needles, or with a large excess of hydrofluoric acid, an acid amorphous gum (Serullas, *Ann. Chem. Phys.* 45, 282).

*Nitrate of Quinine.* — An aqueous solution deposits on evaporation oily drops, which turn waxy, and when kept under water for many days are transformed into very oblique rhombic prisms (Pelletier, Caventou & Dumas). Crystals are obtained only by evaporating the excess of acid and dissolving the residue in water (van Heijningen).

By decomposing mono-acid sulphate of quinine with nitrate of baryta, and leaving the filtrate to evaporate spontaneously, the nitrate is obtained in large, transparent prisms, which give off 4·2 p. c. of water at 100° (2 at. = 4·4 p. c. HO) (Strecker).

| | | at 100°. | | | | Strecker. |
|---|---|---|---|---|---|---|
| 40 | C | 240 | ........ | 62·02 | ........ | 62·1 |
| 3 | N | 42 | ........ | 10·85 | | |
| 25 | H | 25 | ........ | 6·46 | ........ | 6·6 |
| 10 | O | 80 | ........ | 20·67 | | |
| $C^{40}N^2H^{24}O^4,HO,NO^5$ | .... | 387 | ........ | 100·00 | | |

*Fluosilicic alcohol* (xv, 437) in excess precipitates quinine (Knop); *phosphomolybdic acid* (xiii, 164) precipitates it whitish-yellow (Sonnen-schein); *phosphantimonic acid* (xiv, 227) throws down from a solution containing $\frac{1}{1000}$th of quinine, pale-yellow flocks (Schulze); *metatungstic acid* precipitates a still more dilute solution (Scheibler, *J. pr. Chem.* 80, 204).

*Chromate of Quinine.* — a. *Mono-acid.* $C^{40}N^2H^{24}O^4,CrO^3$. — Precipi-tated from an aqueous solution of mono- or bi-acid sulphate of quinine by neutral chromate of potash, in the absence of free acids, and is slowly deposited in tufts of shining golden-yellow needles on recrystallisa-tion. — Permanent in light.    Assumes a green colour when heated above 92°. — Dissolves in 2,400 parts of water at 15°, in 160 parts of boiling water ; in alcohol, but not in ether (André).

b. *Bi-acid.* — $C^{40}N^2H^{24},2CrO^3 + 16aq$. Bichromate of potash throws down from a cold aqueous solution of sulphate of quinine con-taining sulphuric acid, an orange-yellow precipitate consisting of microscopic needles. — Decomposes rapidly in the light.    Turns brown at 60° or 65°, or when boiled with water, evolving oxygen at the same time.    More easily soluble than the mono-acid salt (André, *N. J. Pharm.* 41, 341 ; *Zeitschr. Ch. Pharm.* 5, 649).

*Perchromate of Quinine.* — Formed by adding quinine to an ethereal solution of perchromic acid.    Dries without decomposition.    Dissolves in alcohol, but not in ether (Barreswil, *Compt. rend.* 16, 1085).

*Arseniate of Quinine.* — Needle-shaped prisms, resembling phos-phate of quinine, but less pearly (Pelletier and Caventou).

*Antimonic acid and Quinine.* — Aqueous mono-basic antimoniate of potash (iv. 377, 8) is not precipitated by hydrochlorate of quinine, even on addition of alcohol; but when hot antimoniate of potash is poured into boiling hydrochlorate of quinine, a white precipitate of antimonic acid with a little quinine is thrown down, and the filtrate on cooling and standing deposits nodules containing quinine, potash, and variable quantities of antimonic acid.    Antimoniate of quinine cannot be obtained in this way (C. Graf, *Pharm. Viertelj.* 5, 211).

*Sulphate of Quinine and Iron.* — On leaving a mixture of per-sulphate of iron and sulphate of quinine to evaporate spontaneously, small colourless regular octohedrons separate after some months : they contain sulphuric acid, sesquioxide of iron, and quinine.    The salt tastes slightly bitter, blackens when heated, and carbonises and leaves sesquioxide of iron on ignition (Will., *Ann. Pharm*, 42, 111).    Langeli (*N. J. Br. Arch.* 83, 61) obtained from equivalent quantities of sulphate of quinine and sulphate of iron (ferric sulphate ? Kr.) white prisms of a double-salt easily soluble in water and alcohol.    Baudrimont and Roussin (*N. J. Pharm.* 46, 375) dispute the existence of such a double-salt.

*Quinine with Iodide of Iron?*— A solution of hydriodate of quinine, formed by decomposing 30 parts of sulphate of quinine with iodide of barium, is mixed with a solution of iodide of iron prepared from 12 parts of iodine ; the liquid is concentrated; and the resin which

separates is removed by filtration; alcohol is then added, and the solution is allowed to crystallise. — Long, yellow needles, inodorous, bitter, and tasting of iron. Dissolves in boiling water, in alcohol, and in ether (J. Smedt, *Apoth Zeit.*). Rebillon (*N. Br. Arch.* 103, 365) obtained in this way a fine green resin, insoluble in ether, and containing $C^{40}N^2H^{24}O^4,4FeI$.

Hydrochlorate of quinine behaves like cinchonine with *iodomer-curate of potassium* (Caillot; v. Planta; Delffs), and with chloride of mercury mixed with iodide or bromide of potassium (Groves). — A solution of 6·5 parts of chloride of mercury added to an aqueous solution of 10 parts of hydrochlorate of quinine and 4 parts of iodide of potassium, throws down a yellowish-white precipitate, which crystallises from alcohol, on spontaneous evaporation, in transparent, four-sided prisms. The crystals dissolve with difficulty in water, but more easily in alcohol of 82 p. c., and when mixed with protochloride of tin throw down mercurous iodide. According to Winckler, they consist of hydrochlorate of quinine with iodide of mercury (*Repert.* 35, 62).

*Chloromercurate of Quinine.* — Chloride of mercury throws down from hydrochlorate or acetate of quinine, a dense, pulverulent precipitate, which is not soluble to any great extent in sal-ammoniac, but dissolves easily in hydrochloric acid, and is deposited again from the solution in crystalline globules on standing. Sulphate of quinine is precipitated by chloride of mercury only on addition of chloride of sodium; the precipitate dissolves easily in sal-ammoniac, the solution being permanent (v. Planta). — To prepare the salt, alcoholic quinine containing hydrochloric acid is mixed with an alcoholic solution of mercuric chloride, when, if very strong alcohol is used, a crystalline granular precipitate, or with weak alcohol, a less crystalline precipitate is produced. The precipitate is washed on a filter with alcohol, ether, and water. It dissolves with difficulty in cold water, alcohol and ether, Hinterberger (*Ann. Pharm.* 77, 201). See also Winckler (*Repert.* 35, 57).

|  |  | at 100°. |  |  | Hinterberger. |
|---|---|---|---|---|---|
| 40 C | ............................ | 240 | ........ | 35·92 | ........ 35·80 |
| 2 N | ............................ | 28 | ........ | 4·19 |  |
| 26 H | ............................ | 26 | ........ | 3·89 | ........ 3·89 |
| 4 O | ............................ | 32 | ........ | 4·79 |  |
| 2 Hg | ............................ | 200 | ........ | 29·94 | ........ 29·82 |
| 4 Cl | ............................ | 142 | ........ | 21·27 |  |
| $C^{40}N^2H^{24}O^4,2HCl,2HgCl$ .... | | 668 | ........ | 100·00 |  |

*Nitrate of Quinine* with *Oxide of Silver.* — Alcoholic nitrate of silver throws down from alcoholic quinine a crystalline precipitate containing 1 at. of nitric acid and 1 at. oxide of silver to 1 at. quinine. The precipitate cannot be obtained in a perfectly pure state, on account of the action of nitrate of silver on alcohol (Regnault). When the precipitate after washing with alcohol, is dissolved in boiling water, the solution on cooling solidifies to a jelly, which is transformed into crystals on standing. Loses 1·7 p. c. of water at 110°, after drying over oil of vitriol (1 at. = 1·8 p. c. HO). Dissolves in 286 parts of water at 15° (Strecker).

|  | *Dried.* |  |  | *Strecker.* |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ ..................... | 324 | ........ | 65·59 | |
| $NO^5,O$ ............................. | 62 | ........ | 12·55 | |
| Ag................................. | 108 | ........ | 21·86 | ........ 21·9 |
| $C^{40}N^2H^{24}O^4,AgO,NO^5$.... | 494 | ......... | 100·00 | |

*Terchloride of gold* throws down from solutions of quinine-salts, sulphur- to reddish-yellow precipitates but little soluble in water (v. Planta ; Peschier).

*Chloroplatinate of Quinine.* — Chloride of platinum throws down from quinine-salts a yellowish precipitate which dissolves easily in hydrochloric acid added at the same time (v. Planta). The precipitate is white or yellow, but when an excess of hydrochloric acid is added, yellow and crystalline (Liebig). Orange-yellow crystalline powder, having an acid reaction (Duflos). Neutral (Liebig). Does not lose water at 100°, but gives up 2·37 p. c. at 140° (Gerhardt, *Rev. scient.* 10, 187).— When strongly heated, it evolves hydrochloric acid, blackens, and glows. Dissolves in 1,500 parts of cold, and 120 parts of boiling water, and in 2,000 parts of boiling alcohol of 85°, from which it is deposited on cooling (Duflos, *Schw.* 62, 312).

|  | *Anhydrous.* |  |  |
|---|---|---|---|
| 40 C ..................................... | 240 | ............ | 32·58 |
| 2 N ..................................... | 28 | ............ | 3·81 |
| 26 H ..................................... | 26 | ............ | 3·53 |
| 4 O ..................................... | 32 | ............ | 4·34 |
| 6 Cl..................................... | 213 | ............ | 28·94 |
| 2 Pt..................................... | 197·4 | ............ | 26·80 |
| $C^{40}N^2H^{24}O^4,2HCl,2PtCl^2$.... | 736·4 | ............ | 100·00 |

|  | *Hydrated.* |  |  |  | *Gerhardt. at 100°.* |
|---|---|---|---|---|---|
| 40 C ..................................... | 240 | ........ | 31·81 | ........ | 31·34 |
| 2 N ..................................... | 28 | ........ | 3·71 | ........ | 3·40 |
| 28 H ..................................... | 28 | ........ | 3·72 | ........ | 3·99 |
| 6 O ..................................... | 48 | ........ | 6·36 | ........ | 5·52 |
| 6 Cl ..................................... | 213 | ........ | 28·23 | ........ | 29·49 |
| 2 Pt ..................................... | 197·4 | ........ | 26·17 | ........ | 26·26 |
| $C^{40}N^2H^{24}O^4,2HCl,2PtCl^2 + 2aq.$ .... | 754·4 | ........ | 100·00 | ........ | 100·00 |

Liebig found, on the average, 26·52 p. c. ; Laurent 26·4 p. c. of platinum. Duflos found 25·8 p. c. of platinum, 28·4 of chlorine, and 44·64 of quinine (the anhydrous salt contains by calculation, 43·9 p. c., the hydrated 42·94 p. c. of quinine). Duflos likewise obtained from 10 parts of dried quinine, 22·4 parts of platinum-salt (calc. for anhydrous salt requires 22·72 ; for hydrated salt 23·29 parts).

*Chloride of Iridium and Sodium* throws down from acetate or hydrochlorate, but not from sulphate of quinine, an ochre-yellow to red-brown precipitate, very easily soluble in hydrochloric acid (v. Planta).

*Hydrocyanate of Quinine.* — Quinine triturated and shaken with aqueous hydrocyanic acid dissolves to a yellow liquid (Pezzina, *J. Chim. méd.* 8, 569).

*Hydroferrocyanate of Quinine.* — Resembles the cinchonine-salt (p. 213), and may be obtained in a similar manner (Dollfus). Ferrocyanide of potassium produces in cold aqueous quinine-salts, yellowish-white clouds, which disappear on heating, or on addition of excess of the ferrocyanide, and do not again make their appearance (Bill, *Sill. Amer. J.* (2) 26, 108 ; *J. pr. Chem.* 75, 484).

|  |  |  |  |  | Dollfus. |
|---|---|---|---|---|---|
| 52 C | 312 | ........ | 52·55 | ........ | 52·9 |
| 8 N | 112 | ........ | 18·85 | | |
| 34 H | 34 | ........ | 5·72 | ........ | 6·0 |
| 10 O | 80 | ........ | 13·44 | | |
| 2 Fe | 56 | ........ | 9·44 | ........ | 9·1 |
| $C^{40}N^2H^{24}O^4,Cy^6Fe^2H^4$ + 6 aq. | 594 | ........ | 100·00 | | |

Gerhardt (*Traité* 4, 121) supposes the salt to contain 4 at. water. — Concerning the preparation of this salt as a medicine, see Bertozzi (*J. Pharm.* 19, 45), Ferrari (*Chim. méd.* 11, 361), Geiseler (*N. Br. Arch.* 8, 66), Pelouze (*N. Ann. Chim. Phys.* 6, 67), Landerer (*N. Br. Arch.* 71, 282).

*Hydroferricyanate of Quinine.* — Concentrated aqueous solutions of ferricyanide of potassium throw down from strong aqueous solutions of hydrochlorate of quinine containing a little free hydrochloric acid, golden-yellow, crystalline laminæ, which, after drying, resemble mosaic gold. Does not lose weight at 100°. Dissolves easily in water, and deposits a blue powder on evaporating the solution (Dollfus).

|  |  |  |  |  | Dollfus. |
|---|---|---|---|---|---|
| 52 C | 312 | ........ | 55·11 | ........ | 54·60 |
| 8 N | 112 | ........ | 19·79 | | |
| 30 H | 30 | ........ | 5·30 | ........ | 5·46 |
| 7 O | 56 | ........ | 9·90 | | |
| 2 Fe | 56 | ........ | 9·90 | ........ | 9·86 |
| $C^{40}N^2H^{24}O^4,Cy^6Fe^2H^3$ + 3 aq. | 566 | ........ | 100·00 | | |

Quinine does not form any compound with *cyanide of mercury* (Kohl & Swoboda, *Wien. Akad. Ber.* 9, 252) ; it behaves with that salt in the same manner as cinchonine (Caillot).

*Hydrocyanate of Quinine and Cyanide of Platinum.* — According to Delffs, quinine is not precipitated by platinocyanide of potassium. — Wertheim (*Wien. Akad. Ber.* 1849, 1,263) obtained from sulphate of quinine and platinocyanide of potassium, the compound $C^{40}N^2H^{24}O^4,2HCy,$ $2PtCy + 2$ aq., and from hydrochlorate of quinine and platinid-cyanide of potassium (vi, 49) the salt $C^{40}N^2H^{24}O^4,2HCl,2PtCy^2$. Schwarzenbach describes the following compounds :—

A. $3C^{40}N^2H^{24}O^4,2HCy,2PtCy$. — Platinocyanide of potassium throws down from a solution of quinine in aqueous acetic acid, an abundant white precipitate, which, on standing, is converted partly into fine needles and partly into a resin. The needles melt at 100° to a gum, which also remains transparent on cooling (Schwarzenbach).

|  | Needles. |  |  |  | Schwarzenbach. |
|---|---|---|---|---|---|
| 3 $C^{40}N^3H^{24}O^4,2HCy,2Cy$ | 1078 | ........ | 84·52 | | |
| 2 Pt | 197·4 | ........ | 15·48 | ........ | 16·46 |
| 3 $C^{40}N^2H^{24}O^4,2HCy,2PtCy$ | 1275·4 | ........ | 100·00 | | |

B. $C^{40}N^2H^{24}O^4,2HCy,2PtCy$. — Aqueous platinocyanide of potassium throws down from a clear solution of quinine in not too great an excess of sulphuric acid, a bulky white precipitate, which, in presence of a larger quantity of sulphuric acid, disappears again at first. When left at rest, the precipitate is transformed into tables, warty groups of needles, and a resin (Schwarzenbach).

$a.$ The tables are transparent, quadratic, or oblong, with parallel striæ. On drying they become opaque and waxy, and acquire a faint yellowish-green colour. By picking out the tables, afterwards treating them with boiling water, in which the other forms are not soluble, and rapidly cooling, they are obtained pure and in laminæ. The air-dried tables do not lose weight at 120°, but give up 6·35 p. c. of water at 150°, assuming at the same time a deep-yellow colour, which disappears again almost entirely on cooling.

|  | Tables. |  |  |  | Schwarzenbach. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ ...................................... | 324 | ........ | 48·83 |  |  |
| 2 HCy,2Cy............................................ | 106 | ........ | 15·98 |  |  |
| 2 Pt ................................................... | 197·4 | ........ | 29·75 | ........ | 29·66 |
| 4 HO ................................................... | 36 | ........ | 5·44 | ........ | 6·35 |
| $C^{40}N^2H^{24}O^4,2HCy,2PtCy + HO$.... | 663·4 | ........ | 100·00 |  |  |

$b.$ The warts appear to the naked eye as short prisms or broad needles. They remain behind, together with amorphous white resinous globules, on treating the entire precipitate with boiling water, and may afterwards be dissolved by boiling alcohol, from which they crystallise unchanged on cooling. They turn yellow to orange in sunlight, and when dried over oil of vitriol, contain 30·43 p. c. of platinum, corresponding to the formula $C^{40}N^2H^{24}O^4,2HCy,2PtCy + 2HO$ (by calc. 30·52 p. c. Pt.)

$c.$ The resinous globules are pure white, or translucent and waxy, in the moist state, and insoluble in boiling alcohol. They contain, like $b$, 30·4 p. c. of platinum (Schwarzenbach, *Pharm. Viertelj.* 8, 518).

*Hydrosulphocyanate of Quinine.*—Hydrosulphocyanic acid and quinine form together a yellow resinous salt, and a white salt, which cannot be separated by crystallisation (Dollfus). Strong alcoholic solution of quinine forms with sulphocyanide of potassium, a very small quantity of a white precipitate, which does not dissolve on warming (Artus, *J. pr. Chem.* 8, 253). Neutral acetate of quinine [in concentrated solution only (v. Planta)] immediately forms a white curdy precipitate, which dissolves on heating, and in hot alcohol (O. Henry, *J. Pharm,* 24, 194). Hydrochlorate of quinine produces with sulphocyanide of potassium a dense precipitate and oily drops (v. Planta), or in dilute solutions, microscopic elongated needles (Anderson). Excess of sulphocyanide of potassium throws down from a solution of 1 part of quinine in 400 parts of water containing sulphuric acid, greenish-yellow, delicate needles, which are more quickly precipitated, in the pulverulent form, on violently agitating the liquid (Lepage). Large, regular, pale lemon-yellow crystals of the oblique prismatic system, having the formula $C^{40}N^2H^{24}O^4,2CyHS^2$ (Wertheim, *Wien. Akad. Ber.* 1, 263). After pouring off the mother-liquor, in which it is not soluble on account of the presence of sulphocyanide of potassium, it dissolves easily in water, and especially in alcohol (Lepage, *J. Pharm.* 26, 140).

Chloride of mercury and cyanide of mercury throw down from hydrosulphocyanate of quinine, double salts of the formulæ $3(C^{40}N^2H^{24}O^4,2CyHS^2)+8HgCl$ and $C^{40}N^2H^{24}O^4,2CyHS^2+2HgCy$ (Wertheim).

*Formate of Quinine.* — Crystallises easily in needles resembling the sulphate (L. L. Bonaparte, *J. Chim. méd.* 18, 680).

*Acetate of Quinine.* — Strong acetic acid added to an ethereal solution of quinine throws down a crystalline acetate (Veltmann, *Schw.* 54, 187).

A. *Mono-acid?* — The long silky needles of acetate of quinine give off acetic acid over the water-bath and still more at 140°, when they melt to a nearly colourless glass (Regnault).

|  | *Fused.* |  |  |  | Regnault. |
|---|---|---|---|---|---|
| 44 C | 264 | ........ | 68·77 | ... ... | 69·47 |
| 2 N | 28 | ........ | 7·29 | | |
| 28 H | 28 | ........ | 7·29 | ........ | 7·38 |
| 8 O | 64 | ........ | 16·65 | | |
| $C^{40}N^2H^{24}O^4,C^4H^4O^4$ .... | 384 | ........ | 100·00 | | |

B. *Acid.* — Obtained by the spontaneous evaporation of a solution of quinine in acetic acid, in long silky needles (Schwarzenbach) : on rapid evaporation the whole liquid becomes solid. Faintly acid: dissolves slightly in cold, much more easily in hot water (Pelletier & Caventou). — Contains 69·37 p. c. of quinine. Loses 12·75 p. c. of water (and acetic acid? Kr.) over oil of vitriol. Schwarzenbach (*Pharm. Viertelj.* 8, 518) gives the formula $C^{40}N^2H^{24}O^4,2C^4H^4O^4 + 6aq.$, which requires 65 p. c. of quinine, and 10·8 p. c. of water, and should probably be replaced by $C^{40}N^2H^{24}O^4,2C^4H^4O^4 + 2aq.$ (70·1 p. c. quinine, 3·9 water) (Kr.)

*Oxalate of Quinine.* — *Bibasic?* — Acetate (Regnault) or bi-acid sulphate of quinine is precipitated by oxalate of ammonia or potash, and the precipitate is washed with a little cold water and crystallised from boiling alcohol. — Small, very delicate needles. Dissolves in cold, and more freely in hot water, and very easily in alcohol, especially when hot (Pelletier & Caventou; Regnault; Landerer, *Repert.* 52, 40 ?).

|  | *at 125°.* |  |  |  | Regnault. |
|---|---|---|---|---|---|
| 84 C | 504 | ........ | 68·29 | ........ | 67·03 |
| 4 N | 56 | ........ | 7·59 | | |
| 50 H | 50 | ........ | 6·76 | ........ | 7·03 |
| 16 O | 128 | ........ | 17·36 | | |
| $2C^{40}N^2H^{24}O^4,C^4H^2O^8$ .... | 738 | ........ | 100·00 | | |

B. *Acid?* — Needles easily soluble in water (Pelletier & Caventou).

*Cyanurate of Quinine.* — White amorphous mass (Elderhorst).

*Mellitate of Quinine.* — Alcoholic quinine produces with solution of mellitic acid an abundant white precipitate, which becomes pearly and crystalline when washed with weak alcohol. Does not lose water at 100°, but evolves a little water and ammonia at 130°, turning sulphur-yellow. Dissolves very slightly in cold, and somewhat more freely in

hot water, from which it is deposited as a crystalline powder on cooling (Karmrodt, *Ann. Pharm.* 81, 170).

*Succinate of Quinine* forms pearly prisms (Henry & Delondre).

*Aspartate of Quinine.* — Indistinct crystals, easily soluble in water (Plisson, *J. Pharm.* 15, 273).

*Valerate of Quinine.* — On neutralising alcoholic quinine with a slight excess of valerianic acid, and allowing a mixture of 1 vol. of the liquid with 2 vols. of water to evaporate spontaneously, or at 50° at most, hard rectangular octahedrons or cubes, permanent in the air, are obtained, and by rapid evaporation also needles (Bonaparte). Wittstein employs 1 part of the acid, 60 parts of water, and 3 parts of freshly precipitated quinine. The salt may also be prepared by mixing a solution of 12 parts of valerianic acid in 10 parts of alcohol with a solution of 40 parts of quinine in 140 parts of alcohol of 85 per cent., and evaporating the liquid to crystallisation at a temperature of 30° to 40° (*N. J. Pharm.* 45, 236). Or carbonate of soda is added to slightly alkaline reaction to a mixture of 1 part of valerianic acid and 2 parts of water, and the liquid is added, at a temperature of 48°, to a solution of 2 parts of sulphate of quinine in water containing sulphuric acid, whereupon, on standing for 24 hours, the solution deposits crystals, which must be washed with water at 36° (Chatin, *N. J. Pharm.* [4], 1, 268). Pearly oblique rhomboïdal tables or white needles. Smells of valerianic acid; tastes very bitter, and afterwards of the acid. Neutral (Wittstein). Melts at 90° to a transparent liquid, giving off 3½ p. c. of water, and solidifies to a glass on cooling. When more strongly heated, it gives off valerianic acid. The salt, fused at 90°, dissolves easily in alcohol, and remains on evaporation as an amorphous mass when the alcohol is strong, or in crystals when weaker alcohol is employed (Bonaparte).

The crystals dissolve in 110 parts of cold [96 parts at 18·75° (Abl)], and in 40 parts of boiling water (Wittstein). On boiling, the solution deposits resinous drops of the anhydrous salt, which do not become crystalline on cooling or standing in water, but crystallise from dilute alcohol. The same anhydrous salt is precipitated by valerianic acid from an aqueous solution of the crystals (Bonaparte, *J. Chim. méd.* 18, 680; 19, 330). It dissolves in 6 parts of cold, and in 1 part of boiling alcohol of 80 p. c. (Wittstein, *Repert.* 87, 295). The salt prepared with natural, but not that made with artificial valerianic acid becomes phosphorescent when rubbed, especially after it has effloresced. The two salts also exhibit different crystalline forms (Landerer, *N. Br. Arch.* 119, 240).

| | *Resinous salt.* | | | | Wittstein. |
|---|---|---|---|---|---|
| C⁴⁰N²H²⁴O⁴ ................................. | 324 | ........ | 71·52 | ........ | 71·85 |
| C¹⁰H⁹O³ ..................................... | 93 | ........ | 20·53 | ........ | 20·23 |
| 4 HO ........................................... | 36 | ........ | 7·95 | ........ | 7·92 |
| C⁴⁰N²H²⁴O⁴,C¹⁰H¹⁰O⁴ + 3 aq. .... | 453 | ........ | 100·00 | ........ | 100·00 |

| | *Crystals.* | | | | Wittstein. |
|---|---|---|---|---|---|
| C⁴⁰N²H²⁴O⁴ ................................. | 324 | ........ | 50·47 | ........ | 51·36 |
| C¹⁰H⁹O³ ..................................... | 93 | ........ | 14·49 | ........ | 14·98 |
| 25 HO ......................................... | 225 | ........ | 35·90 | ........ | 33·66 |
| C⁴⁰N²H²⁴O⁴,C¹⁰H¹⁰O⁴ + 24 aq. .... | 642 | ........ | 100·00 | ........ | 100·00 |

Wittstein considers the salt to contain 1 at. water less. See also Riegel (*N. Br. Arch.* 45, 315), Fr. Müller (*N. Br. Arch.* 46, 157), Devay (*N. J. Pharm.* 6, 382).

*Dextrotartrate of Quinine.* — Acid tartrate of potash dissolves quinine in small quantity only and with difficulty; on evaporating the solution a mixture of cream of tartar and a quinine-salt remains (Arppe).

A. *Bibasic.* — When sulphate of quinine is mixed with tartrate of potash a crystalline powder is precipitated. Neutral. Fusible. Tastes bitter. Gives off 1·5 p. c. of water at 145° (Arppe, *J. pr. Chem.* 53, 334).

|  |  |  |  | Arppe. |
|---|---|---|---|---|
| $2C^{40}N^2H^{24}O^4$ ............... | 648 | ........ | 81·27 | ........ 79·0 |
| $C^8H^6O^{12}$ ..................... | 150 | ........ | 18·08 | |
| $2C^{40}N^2H^{24}O^4,C^8H^6O^{12}$ .... | 798 | ........ | 100·00 | |

B. *Mono-acid.* — Equal numbers of atoms of the base and acid are dissolved separately in alcohol, and the solutions are mixed and allowed to crystallise. — Gives off 1·4 p. c. of water at 100°, and the remainder at 160°, in all 4·4 p. c. Decomposes only on prolonged heating to 160° (calc. for $C^{40}N^2H^{24}O^4,C^8H^6O^{12} + 2aq. = 3·67$ p. c. HO) (Pasteur).

*Antitartrate of Quinine.* — See x, 365, and xvii, 217. — Obtained in the same way, and has the same composition as the dextrotartrate; it exhibits, however, a different crystalline form, gives off its water of crystallisation almost entirely at 100°, and dissolves far more freely than that salt, especially in warm water (Pasteur).

*Tartrate of Quinine and Potash.* — Crystals soluble in alcohol (Delondre & Henry).

Quinine, boiled with solution of tartar-emetic, does not yield a double salt analogous to that of quinidine (Stenhouse).

*Croconate* and *Rhodizonate of quinine* resemble the cinchonine-salts (Heller).

*Urate of Quinine.* — Obtained in the same manner as the cinchonine-salt (Elderhorst). Andreae (*Pharm. Viertelj.* 10, 382) uses 1 part of quinine to 1·5 parts of uric acid. — White, amorphous, laminated mass (Elderhorst). Dull white powder, consisting of microscopic prisms. Tastes bitter. Burns, when heated, without melting. Dissolves in 855 parts of cold, and 36·2 parts of boiling water; in 1580 parts of cold, and 45·3 parts of boiling alcohol; still less freely in ether (Andreae).

|  | *at* 100°. |  | | Andreae. |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ ...................... | 324 | ........ | 65·85 | ........ 63 |
| $C^{10}N^4H^4O^6$ ...................... | 168 | ........ | 34·15 | ........ 33 |
| $C^{40}N^2H^{24}O^4,C^{10}N^2H^4O^6$ .... | 492 | ........ | 100·00 | |

Andreae's analysis is doubtful: his formula contains 6 at. water more (Kr). See also Péreyre on urate of quinine (*N. Br. Arch.* 103, 364).

Strong aqueous *pyrogallic acid* throws down from bi-acid sulphate of quinine, a yellow crystalline precipitate (De Luynes, *Compt. rend.* 57,

162). — The compound of quinine with *picrotoxin* resembles the brucine-compound (Pelletier & Couerbe).

*Orcin and (Sulphate of ?) Quinine.* — Quinine behaves towards orcin in the same manner as cinchonine (De Luynes). A moderately dilute aqueous solution of orcin becomes cloudy at first, when a strong aqueous solution of sulphate of quinine is dropped into it, but clear again on further addition of the quinine-salt, after which the solution deposits, when pure orcin is employed, small concentrically arranged needles, but with an impure quinine, an oil which solidifies (Hlasiwetz, *Ann. Pharm.* 134, 290).

*Citrate of Quinine.* Quinine is added to a warm dilute aqueous solution of citric acid till the alkaloïd is no longer dissolved. On cooling and concentrating the solution, fine, white, somewhat silky needles are obtained. Very bitter. Neutral. Dissolves in 820 parts of cold, and 30 parts of boiling water; and in 44 parts of cold, and 3 parts of boiling alcohol of 85 p. c. — Loses 10·6 per cent. in weight at 100° (10 at. = 9·68 p. c. HO), and no more at 145°. Decomposes at 160°, as it begins to melt (Wittstein, *Pharm. Viertelj.* 5, 552; *N. Br. Arch.* 89, 27).

|  |  | at 100°. |  |  |  | Wittstein. |
|---|---|---|---|---|---|---|
| 92 C | ................................... | 552 | ........ | 65·72 | ........ | 66·49 |
| 4 N | ................................... | 56 | ........ | 6·66 | ........ | 6·73 |
| 56 H | ................................... | 56 | ........ | 6·66 | ........ | 6·58 |
| 22 O | ................................... | 176 | ........ | 20·96 | ........ | 20·20 |
| 2 C$^{40}$N$^{2}$H$^{24}$O$^{4}$,C$^{12}$H$^{8}$O$^{14}$ | .... | 840 | ........ | 100·00 | ........ | 100·00 |

Wittstein's formula contains 1 at. water less. See also Galvani (*J. Chim. méd.* 8, 687).

On *citrate of quinine and ferric oxide*, see Fleurot (*N. J. Pharm.* (4) 1, 443).

*Lactate of Quinine.* — Lactic acid saturated with quinine leaves, on evaporation, tufts of silky needles, more easily soluble in water than the sulphate (Bonaparte).
Quinine is not precipitated by *gallic acid* and its salts (Pfaff; Henry); but salts of quinine are rendered turbid by gallic acid which has become yellow from long standing (Wackenroder).

*Picrate of Quinine.* — Alcoholic picric acid forms with alcoholic quinine [with salts of quinine (v. Planta)], even in very dilute solution, a yellow pulverulent precipitate (Kemp, *Repert.* 71, 164). The salt is also obtained from picrate of potash and sulphate of quinine. Yellow; slightly bitter (Bonaparte). Very bitter (Winckler). Nearly insoluble in water; on boiling therewith, the anhydrous salt is deposited in the form of an oily layer, which does not turn crystalline on standing (Bonaparte). Dissolves easily in alcohol, crystallising therefrom (according to Bonaparte, not) in yellow needles (Carey Lea). Dissolves in alcohol (Winckler, *Repert.* 41, 330; Carey Lea, *Sill. Amer. J.* 26, 379; *Chem. Centr.* 1859, 122).

*Anethol and Quinine.* By dissolving 5 parts of quinine and 1 part of anise-oil in boiling alcohol, cooling and concentrating the liquid, and recrystallising the product, shining crystals are obtained. Four-

sided, mostly acute double pyramids, belonging to the oblique prismatic system, with truncated summits. Smells very slightly of anise-oil, more strongly when heated. Tastes of quinine and the oil. Melts in hot water; in the dry state only above 400°, giving off water and oil of anise, amounting together to 21·9 p. c. (by calc. 22·11 p. c.). Dissolves slightly in cold, and freely in boiling alcohol, and very easily in ether (Hesse, *Ann. Pharm.* 123, 382; abstr. *N. Br. Arch.* 115, 169).

|  |  | *Crystals.* |  |  |  | Hesse. |
|---|---|---|---|---|---|---|
| 100 C | ..... | 600 | ..... | 72·11 | ..... | 72·04 |
| 4 N | ..... | 56 | ..... | 6·73 | ..... | 6·48 |
| 64 H | ..... | 64 | ..... | 7·69 | ..... | 7·70 |
| 14 O | ..... | 112 | ..... | 13·47 | ..... | 13·78 |
| $2C^{40}N^2H^{24}O^4,C^{20}H^{12}O^2$ + 4 aq. | ..... | 832 | ..... | 100·00 | ..... | 100·00 |

*Tannate of Quinine.* — Occurs in cinchona-barks, according to Henry & Plisson. Gallo-tannic acid (infusion or tincture of galls) produces a turbidity in very dilute solutions of quinine; from moderately strong solutions it throws down white flocks, which run together when warmed, without dissolving. When the proper proportions are employed, the filtrate produces only a slight blue coloration with ferric salts. — White spongy mass, drying up to a brittle, friable resin. Tasteless and inodorous. Permanent in the air. Contains, according to Delondre & Henry (*N. J. Pharm.* 21, 286), 1 at. quinine to 2 at. tannic acid. Very slightly soluble in water [in 480 parts at 18¾° (Abl)]. Dissolves in ammonia with red colour, easily in alcohol [in 52 parts (Cap & Garot)], and very slightly in ether. The alcoholic solution is precipitated by water; it leaves on evaporation a syrup, which dries up to a brittle gum (N. E. Henry, *J. Pharm.* 11, 334). Dissolves in 130 parts of glycerin, and in 1,200 parts of fat oil (Cap & Garot). By long contact with water, it is converted into soluble gallate of quinine (Lintner, *N. Repert.* 1, 411; Wackenroder, *N. Br. Arch.* 28, 54; Fr. Müller, *N. Br. Arch.* 38, 144; Landerer, *N. Br. Arch.* 83, 1; Barreswil, *N. J. Pharm.* 21, 206).

*Moritannate of Quinine.* — Moritannic acid forms with quinine a pale yellow precipitate. The precipitate produced by moritannate of lime is yellow and non-crystalline. It contains, after drying at 100°, 63·40 p. c. C., 3·89 N., 5·47 H., and 27·24 O. Dissolves slightly in water, and easily in alcohol (Wagner, *J. pr. Chem.* 51, 94 and 103).

*Cinchona-red and Quinine.* — When cinchona-red (xv, 482) is dissolved in alcohol, together with mono-acid sulphate of quinine, and the solution is evaporated, water takes up from the residue acid sulphate of quinine, whilst a compound of cinchona-red and quinine remains undissolved. — Dirty-red powder not tasting bitter at first. — Nearly insoluble in water, but soluble in warm dilute acids, from which it is deposited almost entirely on cooling; it is precipitated also by incomplete neutralisation of the acid solution by alkalis, whilst an excess of alkali separates quinine. — Dissolves easily in alcohol, forming a solution from which lime or magnesia precipitates the whole of the cinchona-red. — According to Henry & Plisson, this compound occurs in cinchona-barks; it remains behind on boiling the bark with water, and forms the greater part of the precipitate produced by cold water in the aqueous extract.

*Kinate of Quinine.* — Occurs in cinchona-barks according to Henry & Plisson. Warm aqueous kinic acid is neutralised with freshly precipitated quinine, and the slightly acid bitter filtrate is evaporated over the water-bath. After moistening with water, the brown residue solidifies to a warty mass, in which small shining crystals are afterwards formed. The salt dissolves easily in water, less freely in alcohol (Henry & Plisson, *Ann. Chim. Phys.* 35, 172; further *J. Pharm.* 15, 405). Contains, according to Baup (*Pogg.* 29, 70), 4 at. water, and dissolves in 3·5 parts of water at 11°, and in 8·88 parts of alcohol.

*Oleate of Quinine.* — Quinine is nearly insoluble in olive oil, and does not saponify when heated with it. When 1 part of quinine is digested with 2 parts of oleic acid for one to two hours at 100°, a solution miscible with fat oils is obtained (Attfield, *Pharm. J. Trans.* 1863, 4, 388; *Pharm. Viertelj.* 13, 230). By the action of quinine on olive oil or *margaric acid*, Tripier (*N. J. Pharm.* 46, 234) obtained soaps miscible in all proportions with oils and fats. On slowly cooling, the very viscid "*Oleomargarate de Quinine*" ultimately crystallises in shining globules.

Quinine is very easily soluble in alcohol (Pelletier & Caventou). It dissolves in nearly all proportions in alcohol of 90 p. c. at 15° (Bussy & Guibourt); in 6 parts of alcohol (Cap & Garot); in 30 parts of cold alcohol of 20° B. (Merck); in about 2 parts of boiling alcohol of sp. gr. 0·820 (Duflos). On spontaneous evaporation of the solution, there remains a resin mixed with a few crystals (van Heijningen). — It dissolves much more easily than cinchonine in *ether* (Pelletier & Caventou); in 60 parts of ether (Merck), remaining in the form of a resin on spontaneous evaporation (van Heijningen). — According to Schlimpert, it dissolves in 6·7 parts of *chloroform* at 17·5°; according to Pettenkofer in 1·8 parts of that liquid. The solution leaves a perfectly transparent residue when evaporated (Herapath). — Quinine dissolves in *benzene* and crystallises from the solution on evaporation (Mansfield). It dissolves in 200 parts of *glycerin*, in 62 parts of *fat oil* (Cap & Garot), in 23·8 parts of *olive oil* (M. Pettenkofer), but according to Pelletier & Caventou only slightly in warm *volatile* and *fat oils*. (See above).

# Quinidine.

$$C^{40}N^2H^{24}O^4 = C^{40}N^2H^{22}O^4,H^2.$$
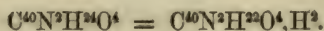
HENRY & DELONDRE. *J. Pharm.* 19, 623; 20, 157.
VAN HEIJNINGEN. *Scheik. Onderzoek,* 5, 4, *Stuk.* 233; *Pharm. Centr.* 1849, 465 and 472; *Ann. Pharm.* 72, 302; *Jahrb. pr. Pharm.* 18, 367; *Repert.* [3] 4, 88; *Chem. Gaz.* 1849, 319 and 325; *N. J. Pharm.* 16, 280 and 446; *Kopp's Jahresber.* 1849, 371.
PASTEUR. *N. J. Pharm.* 23, 123; *Compt. rend.* 36, 26; *J. pr. Chem.* 58, 376; *Kopp's Jahresber.* 1853, 472. — *Compt. rend.* 37, 111.
DE VRIJ. *N. J. Pharm.* 31, 183 and 369; *Pharm. J. Trans.* 16, 401; *Chem. Centr.* 1858, 254; *Kopp's Jahresber.* 1857, 403.
HERAPATH. *Phil. Mag.* [4] 14, 224; *Chem. Gaz.* 1857, 96; *J. pr. Chem.* 72, 104; *Kopp's Jahresber.* 1857, 405. — *Chem. Gaz.* 1858, 56; *J. pr. Chem.* 74, 415. — *Chem. Gaz.* 1858, 70; *J. pr. Chem.*

74, 411; *Kopp's Jahresber.* 1858, 365. — *Chem. Gaz.* 1858, 437; *J. pr. Chem.* 76, 364; *Kopp's Jahresber.* 1858, 368.

KERNER. *Anal. Zeitschr.* 1, 152.

J. STENHOUSE. *Phil. Trans.* 12, 491; *Ann. Pharm.* 129, 15; *Chem. Centr.* 1864, 593.

C. MANN. *Pharm. Viertelj.* 13, 245.

F. KOCH. *N. Jahrb. Pharm.* 22, 240.

*Beta-quinine* (van Heijningen; Koch). Pasteur's *Chinidine*. To be distinguished from the *quinidine* of Winckler and other chemists, which is the same as the cinchonidine of this Handbook. — Discovered in 1833 by Henry & Delondre, who, however, afterwards regarded it as quinine or hydrate of quinine, on the ground of its similar composition. Van Heijningen, and afterwards Pasteur, established the individuality of quinidine. According to the supposition of Pasteur, however, the quinidine examined by van Heijningen was not perfectly pure.

Kerner distinguishes α-, β-, and γ-quinidine.

1. *Alpha-quinidine.* — Formerly met with in commerce mostly as sulphate. — It is obtained from alcohol in large, short, mostly perpendicularly truncated prisms, which effloresce slowly. The sulphate dissolves in 180 to 300 parts of cold water, seldom more freely. — Alpha-quinidine dissolves to a slight extent in luke-warm ether, from which it is crystallised on standing for a short time.

2. *Beta-quinidine.* — Obtained from alcohol in small needles, which effloresce rapidly, and are much more easily soluble in ether than alpha-quinidine. — The sulphate forms brittle, not woolly needles, soluble in 80 to 110 parts of water. From its cold saturated aqueous solution $\frac{1}{4}$ vol. of moderately strong solution of iodide of potassium throws down a pulverulent precipitate, whereas all other cinchona-sulphates, excepting sulphate of quinine, are precipitated thereby in the oleo-resinous form.

3. *Gamma-quinidine.* — Dissolves in ether still more easily than the foregoing. — The sulphate resembles sulphate of quinine, and exhibits the solubility of the corresponding salt of alpha-quinidine; it produces an oleo-resinous precipitate with iodide of potassium.

Koch (*N. Jahrb. Pharm.* 22, 241) finds van Heijningen's quinidine in all cinchona-barks, but in largest quantity in Pitoya bark. He describes it as crystallising in long four-sided prisms, which effloresce rapidly. The sulphate does not give off water at 80°; after drying at 40° to 50° it becomes luminous when pressed in the dark. When exposed in the moist state to light, it assumes a bright green colour. It dissolves in 10 parts of boiling, and in 35 parts of cold water: the solutions become highly fluorescent on addition of sulphuric acid.

De Vrij (*N. Jahrb. Pharm.* 14, 246; further: *Pharm. Viertelj.* 14, 221) obtained from Howard, as a peculiar body, a mixture of quinidine with a not previously recognised cinchona-base, the latter of which he afterwards found in calisaya bark from Java. It forms dull-white, cauliflower-like crystals, which cake together at 35°, assume the consistence of turpentine at 40°, and melt considerably below 100°. The base exerts a left-handed action on polarised light, and dissolves very easily in alcohol and ether. Its hydrate is very bulky, entirely filling the liquid on precipitation. With chlorine-water and ammonia it produces a green coloration, and with iodine and sulphuric acid a

very fine herapathite (p. 311). The hydriodate forms neutral crystals, a solution of which becomes milky, and deposits an oil when concentrated. According to De Vrij, this substance is probably identical with van Heijningen's $\gamma$-quinine (p. 273).

According to Herapath (*Phil. Mag.* (4) 14, 224; *Kopp's Jahresb.* 1857, 405) there exists, together with quinidine, another base which forms prismatic crystals, like quinidine and cinchonidine. With sulphuric acid and iodine it forms crystals which appear of a deep olive-green by reflected, and orange-yellow by transmitted light. Thin plates cut at right angles to the axis are brown or black by polarised light. The solution of this base in chloroform yields on evaporation a gummy residue, which immediately exhibits a deep blue-green fluorescence in Canada balsam.

Hlasiwetz (*Ann. Pharm.* 77, 49) describes as *cinchotine*, fine rhomboïdal crystals of considerable size and diamond-like lustre, which he obtained from the alcoholic mother-liquor of commercial cinchonine. The crystals dissolve easily in ether, become opaque when warmed, then melt, and solidify to an amorphous mass on cooling. They yield no sublimate either alone or in a stream of hydrogen or ammonia-gas. Hirschberg (*Pharm. Centr.* 1851, 175; *Kopp's Jahresber.* 1851, 467) believes that these crystals are sometimes formed instead of cinchonine in the manufacture of cinchonine, and are always obtained, together with cinchonine, in working brown cinchona-barks. According to Delffs, they are identical with quinidine (*N. Jahrb. Pharm.* 11, 321; *Chem. Centr.* 1859, 751). Schabus (*Bestimm.* 1855, 171) found them to belong to the oblique prismatic system. Octahedron, having the anterior and posterior summits truncated by a face $t$ (fig. 43), the upper summits by the base (fig. 42); the crystals are elongated in the transverse axis. Inclination of $a$ and $a'$ to the base = 118° 30'; $a'' : t =$ 108° 18'; $a''$ to base = 109° 28'; base to $t =$ 102° 40'. The faces are smooth and even; those of the octahedrons slightly shining.

*Occurrence of Quinidine.* — In cinchona-barks, especially in yellow barks (which? Kr.), together with quinine and cinchonine (Henry & Delondre). A cinchona-bark from Bogota contained little quinine or cinchonine, but 2·5 to 2·6 p. c. of quinidine (Mettenheimer, *Jahrb. pr. Pharm.* 24, 229; *Pharm. Viertelj.* 1, 586); Reichel (Wiggers, 418), however, found 0·56 p. c. at most; Pereira 1·17 p. c., and Hindsley ¼th per cent. of quinidine in *China Bogota.* — According to Howard, quinidine occurs especially in certain varieties of *Cinchona condaminea*, more especially in *var. pitayensis* (De Vrij). According to Henkel (*N. Repert.* 13, 200) in *Cinchona nitida*, together with cinchonine and a little quinine.

The root-bark of *Cinchona Calisaya* contains quinidine and a little quinine (Howard, *Repert.* 13, 204). — The red bark of 18 months or younger plants of *Cinchona officinalis*, *C. micrantha* and *C. succirubra*, grown in the East Indies, contained 6 p. c. of alkaloïds, of which about 4·1 p. c. consisted of quinidine, cinchonidine, and quinine, and 0·9 p. c. of cinchonicine with traces of cinchonine (Howard, *Pharm. Trans.* 5, 368; *Chem. Centr.* 1864, 655).

The quinidine of commerce is, for the most part, a mixture of quinidine and a second base (Pasteur). The specimens of quinidine in the London Exhibition of

1855 [? Paris, 1855, or London, 1862] were exclusively cinchonidine rendered impure by quinine (De Vrij).

*Preparation.* 1. The yellow bitter mother-liquors which are obtained in the manufacture of quinine, and remain on distilling off the alcohol and separating the quinine, contain a large quantity of quinidine, which is precipitated partially only by ammonia in white flocks running together to a yellow resin. From the strongly ammoniacal filtrate caustic soda throws down a mixture of quinidine, resin, and lime (Henry & Delondre).

2. *From the commercial quinoïdine.* — That soluble in ether answers the purpose best (Delffs). — 100 grammes of commercial quinoïdine are dissolved in as small a quantity of ether as possible ; the brown-yellow solution is filtered, decolorised with animal charcoal, and mixed with $\frac{1}{10}$th of its volume of alcohol of 90 p. c. ; and the greater part of the liquid is allowed to evaporate spontaneously ; it then deposits a large quantity of crystals, which are purified by washing with alcohol. After neutralising with dilute sulphuric acid, the mother-liquor yields at first a further quantity of quinidine as sulphate, and afterwards sulphate of quinine (van Heijningen). In this way 50 to 60 p. c. of quinidine is obtained from quinoïdine.

De Vrij dissolves commercial quinoïdine in the smallest possible quantity of alcohol, and neutralises the solution with aqueous hydriodic acid, whereupon crystals of hydriodate of quinidine, amounting to 23 p. c. of the quinoïdine employed, soon make their appearance.

The sulphate of quinidine is decomposed by dissolving it in dilute sulphuric acid and precipitating with ammonia. The washed and dried precipitate is dissolved in 90 p. c. alcohol, from which hydrated quinidine crystallises on slow evaporation (van Heijningen).

When recrystallised commercial quinidine is exposed to warm air the crystals of quinidine effloresce, whilst those of cinchonidine retain their transparency (Pasteur).

When a very dilute aqueous solution of a pure quinine-salt is precipitated by ammonia, and the granular resinous precipitate is washed, dissolved in warm alcohol of 32°, and mixed with so much water that the solution is rendered milky, and the liquid is then exposed to the air, the hydrate which is thrown down at first in the form of a fluid resin, is converted into fine radiated crystals, and the sides of the vessel become covered with needles. The crystals are efflorescent, long, six-sided prisms, which soften when heated, and melt to a yellow transparent resin at 150° to 155° (Henry & Delondre). This statement probably refers to quinidine, which Henry & Delondre at that time regarded as very pure quinine (Kr.).

*Properties.* The hydrated crystals (see below) lose their water of crystallisation at 110° to 130°, becoming anhydrous. The salt melts at 160° to a transparent liquid, which solidifies to a resin on cooling. Has a slightly alkaline reaction in aqueous solution (van Heijningen ; Henry & Delondre). Very bitter, especially in acid or alcoholic solution (Henry & Delondre). Exerts a right-handed action on polarised light $[\alpha]$ j = 250·75° (Pasteur ; Herapath). According to Bouchardat & Boudet (*N. J. Pharm.* 23, 288) Henry & Delondre's quinidine produces a left-handed rotation. Occurs in the urine after being taken (Herapath).

| | | Dried. | | | Henry & Delondre. | | van Heijningen. mean. | | Stenhouse |
|---|---|---|---|---|---|---|---|---|---|
| 40 C | 240 | ........ | 74·07 | ........ | 74·44 | ........ | 74·08 | ........ | 74·04 |
| 2 N | 28 | ........ | 8·64 | ........ | 8·68 | ........ | 8·55 | | |
| 24 H | 24 | ........ | 7·41 | ........ | 7·10 | ........ | 7·44 | ........ | 7·71 |
| 4 O | 32 | ........ | 9·88 | ........ | 9·78 | ........ | 9·93 | | |
| C⁴⁰N²H²⁴O⁴ | 324 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | | |

Isomeric with quinine (Henry & Delondre).

*Decompositions.* 1. Quinidine *burns* on platinum foil with an aromatic odour like that of melilot, a part volatilising (van Heijningen; Henry & Delondre). — 2. Quinidine-salts, when *heated*, are converted into salts of quinicine (Pasteur). See page 302. — *Chlorine-water* and *ammonia* colour quinidine green, even in solutions containing only $\frac{1}{5000}$th of the alkaloïd (Pasteur; Herapath). In concentrated solutions a precipitate is formed, which is not the case with quinine (Herapath). *Chlorine-water, ferricyanide of potassium,* and *ammonia,* added in succession to salts of quinidine, produce a permanent bulky precipitate, whilst the same reagents produce, with salts of quinine, only a red coloration which quickly disappears (Schwarzer, *N. Jahrb. Pharm.* 23, 348). — Quinidine forms with *iodine* and *sulphuric acid* a compound corresponding to Herapathite (p. 313). — Quinidine heated for half an hour with *iodide of ethyl,* forms hydriodate of ethyl-quinidine (Stenhouse).

*Combinations.* — *With Water.* — A. *Hydrated Quinidine.* — Obtained from ether or warm alcohol in transparent, clinorhombic crystals, which turn white and opaque in the air (van Heijningen). Broad distinct crystals (Stenhouse). White needles (Henry & Delondre). Remains as a transparent gum (hydrated? Kr.) on evaporating a solution in chloroform (Herapath).

The crystals effloresce rapidly in the air (Henry & Delondre; Pasteur). They lose 10·8 p. c. of water at 110° to 130° (van Heijningen), 5·8 p. c. at 130° (Henry & Delondre).

| | | Crystals. | | | van Heijningen. |
|---|---|---|---|---|---|
| C⁴⁰N²H²⁴O⁴ | 324 | ........ | 90·00 | | |
| 4HO | 36 | ........ | 10·00 | ........ | 10·8 |
| C⁴⁰N²H²⁴O⁴,4HO | 360 | ........ | 100·00 | | |

B. *Aqueous solution.* — Quinidine (crystallised? Kr.) dissolves in 1,500 parts of water at 8°, and in 750 parts of boiling water, from which the greater part is deposited in crystals on cooling (van Heijningen; De Vrij). This crystallisation was not observed by Delffs (*N. Jahrb. Pharm.* 11, 321). The cold aqueous solution becomes milky on the addition of a large quantity of alkali. It is rendered brown by tincture of iodine, and is not precipitated by nitrate of silver or mercuric nitrate.

*With Acids.* Quinidine forms mono- and bi-acid salts (van Heijningen), which resemble the salts of quinine, but are, for the most part, more easily crystallisable (Henry & Delondre). The sulphates, the mono-acid hydrochlorate, and the oxalate exert a powerful action on polarised light (Herapath). The salts are in some cases more

soluble than the corresponding salts of quinine, so that oxalic, acetic, and tartaric acids do not precipitate soluble quinidine-salts. The hydrochlorate and nitrate are less soluble (van Heijningen). With excess of acid the salts are as highly fluorescent as those of quinine (Herapath; Stenhouse). The precipitate thrown down by ammonia in their solutions dissolves far less easily than quinine, but more easily than cinchonidine, in excess of ammonia (Kerner). Tartaric acid does not prevent the precipitation of quinidine by bicarbonate of soda (Riegel, *Jahrb. pr. Pharm.* 25, 340).

*Sulphate of Quinidine.* — A. *Mono-acid.* — Resembles sulphate of quinine, but is softer and less woolly to the touch. Gives off its water of crystallisation at 130° (van Heijningen).

The salt dissolves in 350 parts of water at 10°, and in 32 parts of absolute alcohol (van Heijningen). It dissolves in cold aqueous solutions of Glauber's salt and Rochelle salt so freely, that the presence of quinidine is indicated in the filtrate by ammonia, and by chlorine-water and ammonia (C. Mann). A solution in boiling water is greenish (Herapath).

|  | *at 100°.* | | | van Heijningen. |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ | 324 | ........ | 75·88 | |
| $SO^3$ | 40 | ........ | 9·37 | ........ 9·58 |
| HO | 9 | ........ | 2·11 | |
| 6 aq. | 54 | ........ | 12·64 | ........ 12·84 |
| $C^{40}N^2H^{24}O^4,HO,SO^3 + 6$ aq. | 427 | ........ | 100·00 | |

B. *Bi-acid.* — Crystals, very easily soluble in cold water (van Heijningen). Circular tufts of fine needles. When one of the tufts is laid upon a plate of tourmaline covered with selenite, opposite quarters of the circle appear of the same colour, whilst the intermediate quarters exhibit the complementary colour (green and red or yellow and blue) (Herapath).

*Hydriodate of Quinidine.* — A. *Mono-acid.* Iodide of potassium throws down from sulphate [or hydrobromate (De Vrij)] of quinidine, a white granular precipitate, which crystallises from boiling water in needles (Henry & Delondre). Small, white, very hard and heavy crystals. Dissolves in 1,250 parts of water at 15°, and crystallises easily from a boiling saturated solution on cooling (De Vrij).

B. *Bi-acid.* — Fine, pale-yellow salt, soluble in 90 parts of water at 15° (De Vrij).

Quinidine behaves towards *biniodide of potassium* in the same manner as quinine (Bouchardat & Boudet). Iodine dissolved in hydriodic acid throws down from all salts of quinidine an abundant red-brown precipitate (De Vrij).

*Hydrobromate of Quinidine.* — The mono-acid salt resembles the hydriodate, but dissolves in 200 parts of water at 14°. It is precipitated from the hydrochlorate by bromide of potassium (De Vrij).

*Hydrochlorate of Quinidine.* — A. *Mono-acid.* — Chloride of sodium throws down from cold saturated aqueous solutions of sulphate of quinidine, light woolly crystals, resembling hydrochlorate of quinine (De Vrij). — By dissolving quinidine in aqueous hydrochloric acid, fine

transparent crystals are obtained, which lose 4·79 p. c. of water at 120°, (2 at. = 49 p. c. HO). Dissolves easily in water and in alcohol (van Heijningen).

|  | at 130°. |  |  | van Heijningen. |
|---|---|---|---|---|
| C$^{40}$N$^2$H$^{24}$O$^4$ ............ | 324 | ........ | 89·87 | |
| HCl ........................ | 36·5 | ........ | 10·13 | ........ 9.48 |
| C$^{40}$N$^2$H$^{24}$O$^4$,HCl .... | 360·5 | ........ | 100·00 | |

B. *Bi-acid.* — In a current of hydrochloric acid gas, 100 parts of quinidine take up 22·52 parts of the acid (calc. for C$^{40}$N$^2$H$^{24}$O$^4$,2HCl = 21·91 parts); a solution of the compound in water yields large, fine crystals (van Heijningen).

*Nitrate of Quinidine.* — When quinidine is added in excess to nitric acid, and the solution is filtered, large, flat, shining crystals separate (van Heijningen).

*Chloride of Zinc with Mono- and Bi-acid Hydrochlorate of Quinidine.* — Slightly acid solutions of chloride of zinc throw down from alcoholic quinidine a granular powder, slightly soluble in cold and in boiling water, but easily soluble in dilute hydrochloric acid. The easily formed solution of the precipitate in alcohol of 50 p. c. yields crystals resembling calcspar, and containing 26·7 p. c. of chlorine (C$^{40}$N$^2$H$^{24}$O$^4$,2HCl + 2ZnCl = 26·65 p. c. Cl); when re-crystallised, the compound gives up hydrochloric acid and chloride of zinc, and is ultimately transformed into large hexagonal tables and prisms. The latter contain 7·44 p. c. of zinc at 100°, and are, therefore, C$^{40}$N$^2$H$^{24}$O$^4$,HCl + ZnCl (calc. = 7·58 p. c. Zn) (Stenhouse).

*Chloromercurate of Quinidine.* — Precipitated as a white powder on mixing hydrochlorate of quinidine and chloride of mercury, and obtained in pearly laminæ from a solution in boiling alcohol. — Melts under boiling water. Dissolves slightly in cold, more easily in hot water, and especially in water containing hydrochloric acid; from the last solvent it is occasionally deposited in the form of a resin (Stenhouse).

|  | at 100°. |  |  | Stenhouse. |
|---|---|---|---|---|
| C$^{40}$N$^2$H$^{24}$O$^4$ ...................... | 324 | ........ | 60·84 | |
| 2H,Hg ................................ | 102 | ........ | 19·15 | |
| 3 Cl .................................... | 106·5 | ........ | 20·01 | ........ 20·01 |
| C$^{40}$N$^2$H$^{24}$O$^4$,2HCl,HgCl.... | 532·5 | ........ | 100·00 | |

*Quinidine with Nitrate of Silver.* — Alcoholic quinidine solidifies on addition of nitrate of silver, from formation of fine needles, which are to be washed with cold water and recrystallised from boiling water containing nitric acid. — Fine silky needles, having a silvery lustre when dry. Decomposes when recrystallised from alcohol, with separation of silver (Stenhouse).

|  | at 100°. |  |  | Stenhouse. |
|---|---|---|---|---|
| C$^{40}$N$^2$H$^{24}$O$^4$ ...................... | 324 | ........ | 65·59 | |
| NO$^6$ ............................... | 62 | ........ | 12·55 | |
| Ag ..................................... | 108 | ........ | 21·86 | ........ 21·59 |
| C$^{40}$N$^2$H$^{24}$O$^4$,AgO,NO$^5$ .... | 494 | ........ | 100·00 | |

*Chloroaurate of Quinidine.* — Thrown down from cold hydrochlorate

of quinidine by excess of terchloride of gold, as a pale-yellow precipitate, which is to be dried in a vacuum, and afterwards at 100°. Melts at 115°, or on boiling with water, and turns brown (Stenhouse).

|  | at 100°. |  |  | Stenhouse. |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ .......................... | 324 | ........ | 32·29 |  |
| 2 HCl,6Cl ................................ | 286 | ........ | 28·52 |  |
| 2 Au ...................................... | 393·2 | ........ | 39·19 | ........ 39·15 |
| $C^{40}N^2H^{24}O^4,2HCl,2AuCl^3$ .... | 1003·2 | ........ | 100·00 |  |

*Chloroplatinate of Quinidine.* — Separates immediately in the form of a precipitate on adding bichloride of platinum to a strong cold solution of hydrochlorate of quinidine; from hot or dilute solutions crystals are obtained after some time. When recrystallised from boiling dilute hydrochloric acid, it forms shining, irregular crystals. — Decomposes at 200°, with an odour of white-thorn. Dissolves with difficulty in water either cold or boiling (Stenhouse). Gives off 4·86 p. c. of water at 100°.

|  | Air-dried. |  |  | van Heijningen. |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ .......................... | 324 | ........ | 41·96 | ........ 42·55 |
| 2 H ...................................... | 2 | ........ | 0·25 |  |
| 6 Cl ..................................... | 213 | ........ | 27·57 | ........ 27·85 |
| 2 Pt ..................................... | 197·4 | ........ | 25·56 | ........ 25·65 |
| 4 HO ................................... | 36 | ........ | 4·66 | ........ 4·86 |
| $C^{40}N^2H^{24}O^4,2HCl,2PtCl^2 + 4$ aq. .... | 772·4 | ........ | 100·00 |  |

The salt dried at 150° contains 26·66 p. c. of platinum (Stenhouse) (calc. = 26·67 p. c.).

Quinidine is coloured pale-yellow by *platinocyanide of potassium* (Delffs).

*Acetate of Quinidine.* — Crystallises from the syrupy solution on standing for some days, in fine, transparent crystals (van Heijningen). Turns blue litmus paper red, and red blue (De Vrij).

*Oxalate of Quinidine.* — A. *Bibasic.* — Small brittle crystals, obtained by neutralising oxalic acid with quinidine. Nearly insoluble in cold, but freely soluble in boiling water (Stenhouse).

|  | at 100°. |  |  | Stenhouse. |
|---|---|---|---|---|
| 84 C .......................... | 504 | ........ | 66·67 | ........ 66·45 |
| 4 N .......................... | 56 | ........ | 7·41 |  |
| 52 H .......................... | 52 | ........ | 6·88 | ........ 7·17 |
| 18 O .......................... | 144 | ........ | 19·04 |  |
| $2C^{40}N^2H^{24}O^4,C^4H^2O^8 + 2$ aq. .... | 756 | ........ | 100·00 |  |

B. *Mono-acid.* — Obtained by van Heijningen in the same way as the bibasic salt was obtained by Stenhouse, and not by double decomposition. — Pearly crystals, giving off 4·32 p. c. of water at 120° (van Heijningen).

|  | Crystals. |  |  | van Heijningen. |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$.......................... | 324 | ........ | 77·89 |  |
| $C^4H^2O^8$ .......................... | 74 | ........ | 17·79 | ........ 19·83 |
| 2 HO .......................... | 18 | ........ | 4·32 | ........ 4·32 |
| $C^{40}N^2H^{24}O^4,C^4H^2O^8 + 2$ aq. .... | 416 | ........ | 100·00 |  |

*Succinate of Quinidine* forms pearly prisms (Henry & Delondre).

*Tartrate of Quinidine.* — Pearly crystals, obtained in the same way as the oxalate (van Heijningen). The dextrotartrate and antitartrate undergo the same transformation as the quinine-salts when heated (Pasteur).

*Tartrate of Quinidine and Potash?* — Quinidine and cream of tartar yield crystals soluble in alcohol (Henry & Delondre).

*Tartrate of Antimony and Quinidine.* — 1. Mono-acid tartrate of quinidine is boiled for some hours with freshly precipitated oxide of antimony, and the filtrate is left to evaporate. — 2. Powdered quinidine is added to a cold saturated aqueous solution of tartar-emetic; the liquid is heated to boiling; and the excess of quinidine, together with the precipitated oxide of antimony, is separated by filtration from the solution of the double salt and neutral tartrate of potash. — Long, slender needles, which, after drying in a vacuum, lose $\frac{1}{2}$ to 1 per cent. of water at 100°. Dissolves slightly in cold, easily in hot water, and easily also in boiling alcohol, from which it crystallises (Stenhouse).

|        |       |       |        | Stenhouse. In vacuo. |        | mean. at 100°. |
|--------|-------|-------|--------|--------|--------|--------|
| 48 C   | 288   | ........ | 47·28 | ........ | 47·87 | ........ | 47·51 |
| 2 N    | 28    | ........ | 4·59  |        |       |        |
| 29 H   | 29    | ........ | 4·76  | ........ | 5·53 | ........ | 4·87 |
| 18 O   | 144   | ........ | 23·63 |        |       |        |
| Sb     | 120·3 | ........ | 19·74 | ........ | 20·53 | ........ | 19·61 |
| C⁴⁰N²H²⁴O⁴,HO,SbO³,C⁸H⁴O¹⁰.... | 609·3 | ........ | 100·00 |        |       |        |

*Picrate of Quinidine.* — A solution of quinidine in boiling picric acid deposits, on cooling, a resin which does not crystallise from solution in alcohol on evaporation (Stenhouse).

Aqueous quinidine is precipitated white by *tannic acid* (van Heijningen). — Quinidine behaves like quinine with *oleic acid* and *olive oil* (Attfield).

Quinidine dissolves in 45 parts of absolute *alcohol* at 8°, and in 3·7 parts of boiling alcohol (van Heijningen). It is deposited from solution in alcohol of 15° to 18° Baumé, in crystals, or in the form of a resin which crystallises when treated with aqueous alcohol (Henry & Delondre). — Dissolves in 90 parts of *ether* (van Heijningen).

# Quinicine.

$$C^{40}N^2H^{24}O^4 = C^{40}N^2H^{22}O^4,H^2.$$
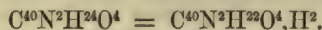
PASTEUR.   *Compt. rend.* 37, 111, and 166.

On heating a salt of quinine or of quinidine, especially a salt which melts below the temperature of decomposition, one and the same isomeric product, quinicine, is formed in both cases. Quinicine exerts a right-handed rotatory action on polarised light, and resembles cinchonicine (p. 230), except in composition; a solution of quinicine in aqueous racemic acid, however, deposits at first chiefly the dextro-

tartrate, whilst the antitartrate accumulates in the mother-liquor.— Quinicine is coloured green by chlorine-water and ammonia, though less intensely than quinine (Herapath).

*Appendix to Quinidine and Quinicine.*

## Quinoïdine.

SERTÜRNER. *Hufel & Osann's Journ.* 1829, 95.
THIEL. *Mag. Pharm.* 2, 83.
BUCHHOLZ. *N. Tr.* 6, 2, 94.
GRUNER. *Br. Arch.* 12, 156.
GEIGER. *Mag. Pharm.* 7, 44 ; *Handb. der Pharm.* 4 ed. 1, 1048.
HENRY & DELONDRE. *J. Pharm.* 16, 144 ; *N. Tr.* 22, 1, 244 ; abstr. *Schw.* 60, 343.
GUIBOURT. *J. Chim. méd.* 6, 357 ; abstr. *Schw.* 60, 245.
DUFLOS. *Schw.* 62, 308.
LIEBIG. *Ann. Pharm.* 58, 348.
WINCKLER. *Jahrb. pr. Pharm.* 7, 65 ; 13, 361 ; 15, 281 ; *Repert.* 98, 391 ; *Jahrb. pr. Pharm.* 17, 32 ; 18, 367 ; *Kopp's Jahresber.* 1849, 373.

Sertürner recognised the basic nature of quinoïdine, and distinguished it from quinine and cinchonine as a peculiar uncrystallisable base. He is, therefore, to be regarded as the discoverer of amorphous quinine.

Quinoïdine occurs in commerce as a brown resinous mass, which is obtained in the manufacture of quinine and cinchonine by precipitating the brown uncrystallisable mother-liquors with ammonia or potash, and washing and drying the precipitate. Sertürner's quinoïdine was obtained in a similar manner.

The product obtained by evaporating the mother-liquors of sulphate of quinine to dryness also occurs in commerce as quinoïdine (Geiger).

Concerning the adulterations of quinoïdine, and the detection thereof, see Walz (*Jahr. pr. Pharm.* 19, 270) ; R. Lehmann (*N. Br. Arch.* 61, 132) ; Volland (*N. Br. Arch.* 61, 136) ; Overbeck (*N. Br. Arch.* 61, 304) ; Wessel & Wolpert (*N. Br. Arch.* 61, 306, and 62, 308) ; Winckler (*Jahrb. pr. Pharm.* 18, 371).

There appear to be two kinds of quinoïdine, which may be distinguished as follows:—

a. *Containing quinidine, with smaller quantities of quinine, cinchonine, and resin.* Dissolves freely in ether. Obtained from inferior kinds of cinchona-bark, but not from *Cinchona regia* or *C. flava dura* (Winckler).

Commercial quinoïdine was found to contain 72·75 p. c. C., 7·30 H., and 8·68 N., and was separable into 3 p. c. quinine, 6 to 8 p. c. cinchonine, and 50 to 60 p. c. quinidine. When this body is dissolved in dilute sulphuric acid, and the solution is warmed for some hours, so that it acquires a dark-brown colour, it yields on cooling few or no crystals of sulphate of quinidine. On pouring the solution thus treated into a large quantity of water, filtering from the black precipitate which is deposited, precipitating the filtrate with ammonia, and dissolving the precipitate in sulphuric acid, crystals of sulphate of

quinidine are obtained. — Quinoïdine contains also amorphous quinine (van Heijningen).

Duflos and Roder, who believed they had obtained sulphate of quinine from quinoïdine, appear to have investigated a similar quinoïdine, and to have confounded quinine with quinidine.

Roder (*J. Chim. méd.* 25, 184) dissolves quinoïdine in 4 parts of alcohol, adds gradually $1\frac{1}{2}$ parts of chloride of tin dissolved in 2 parts of water, whereby a resinous precipitate is thrown down, and precipitates the decanted liquid with ammonia. The grey-white precipitate is washed, again treated in the same way as the original quinoïdine, and precipitated with ammonia ; and the precipitate is dissolved in alcohol, and combined with sulphuric acid, whereupon the sulphate crystallises. Winckler did not obtain crystals by this process.

Duflos (*Schw.* 62, 308) mixes the uncrystallisable mother-liquor evaporated to a syrup with half its weight of oil of vitriol, with constant stirring. After standing for some hours, the liquid is diluted with water, neutralised almost completely with milk of lime, strained, and pressed ; and the filtrate is digested with animal charcoal. The liquid, again filtered, is precipitated with milk of lime, and the precipitate is collected, dried, and exhausted by boiling with alcohol of 80 p.c. The tincture distilled to $\frac{1}{3}$rd of its bulk, deposits crystals of cinchonine on standing, whilst the mother-liquor, neutralised with sulphuric acid, diluted with water, and freed from alcohol by distillation, yields sulphate of quinine [quinidine (Kr.)].

b. *Quinoïdine consisting chiefly of uncrystallisable transformation-products of the Cinchona-bases.* — Dissolves to the extent of 20 to 25 p.c. and often only to 5 or 10 p. c. in pure ether (Winckler).

When true *Cinchona regia* or *Cinchona flava dura* is employed in the preparation of quinine, the brown-red mother-liquor contains neither quinidine nor cinchonidine, but traces only of amorphous quinine, cinchonine, and a red-brown resin, insoluble in ether (Winckler).

Quinoïdine is always a transformation-product of the cinchona-alkaloïds, being formed either in their preparation or in the drying of the cinchona-tree. In the latter case the change is produced especially by sunlight, since the salts of quinine and cinchonine turn red-brown in the sun (Pasteur). — Quinoïdine is a mixture of amorphous quinine and two non-bitter resins, and does not contain any peculiar alkaloïd. (Winckler).

On treating quinoïdine with commercial ether, evaporating the solution, and treating the residue with pure ether, a portion only is dissolved. The undissolved portion behaves exactly like the product obtained by the action of oil of vitriol on cinchonine (p. 203) ; it forms also a yellow, loose, pulverulent platinum-salt, containing 22·5 to 23·5 p. c. of platinum (Winckler).

Quinoïdine neutralises acids, and yields a large quantity of chinoline when distilled with caustic potash ; but its salts are uncrystallisable. On dissolving it in acids, precipitating the solution by ammonia or carbonate of soda, agitating the precipitate with ether, which dissolves it almost completely, and evaporating the ethereal solution, an amorphous residue, resembling the original quinoïdine, remains. The same amorphous quinine is obtained also by warming quinoïdine with aqueous sulphate of copper (which dissolves it, with separation of oxide of copper), removing the copper by means of hydrosulphuric

acid, and precipitating the alkaloïd with an alkali. It contains, on the average, 73·65 p. c. C., 7·63 H., and 8·79 N. It is insoluble in cold, but slightly soluble in hot water, and neutralises acids, forming uncrystallisable salts, from which it is precipitated by ammonia and alkaline carbonates. The platinum-salt resembles the corresponding quinine-compound, and contains 32·44 p. c. C., 3·86 H., and 26·37 Pt. This amorphous quinine dissolves in alcohol, from which it is precipitated as a resin by water; it is soluble also in ether (Liebig). Powerfully antifebrile (Hruschauer, *Ann. Pharm.* 60, 116).

Winckler's *amorphous quinine* is obtained from quinoïdine or from the mother-liquors of the sulphate.

1. *From the mother-liquors of Sulphate of Quinine.* — The mother-liquors, diluted with hot water, are saturated with sulphate of soda, and precipitated in portions by carbonate of soda so long as a dark-brown resin is separated thereby, and till the super-natant liquid appears of a wine-yellow colour. The precipitated resin contains only small quantities of cinchonine and amorphous quinine, which may be extracted by successive treatment with ether and alcohol. — From the wine-yellow liquid, excess of carbonate of soda throws down white flocks, running together to a resin, and con-taining cinchonine and amorphous quinine, the former of which may be separated by repeatedly dissolving the precipitate in ether-alcohol, leaving the solution to crystallise, precipitating the alcoholic solution with a large quantity of ether, and dissolving the precipitate in pure ether (Winckler).

2. *From Quinoïdine.* — Quinoïdine is mixed with its own weight of oil of vitriol and allowed to stand at a temperature not exceeding 37°, till the syrup becomes perfectly homogeneous, for which purpose several days are required when large quantities are employed. The liquid is then diluted and filtered, the hot filtrate is precipitated with carbonate of soda, and the precipitate washed with hot water. The precipitate is still coloured: it is therefore suspended in 12 parts of water; acetic acid is added till solution is nearly complete; the liquid is decolorised with animal charcoal and afterwards precipitated by ammonia; these operations are repeated; and the product is washed and dried. The pale-yellow resin, easily triturable to an electric powder, still contains cinchonine, which remains behind on dissolving in ether. The portion soluble in ether forms with sulphuric acid a salt which is distinguished from sulphate of quinine by its ready solubility. When this body is freed from admixed quinine as far as possible by crystallisation, and then mixed, in neutral solution, with phosphate of soda (whereby only a very little phosphate of quinine is precipitated on standing for several days) two layers are formed, from the lower of which ammonia throws down amorphous quinine.

By the fractional precipitation of its hydrochloric solution with carbonate of soda, quinoïdine may be resolved into a resin insoluble in alcohol, and a pale-yellow portion richer in alkaloïds.

When amorphous quinine is precipitated from the sulphate by car-bonate of soda, the white flocks immediately run together to a hard yellow resin, which, after washing with hot water and drying over the water-bath, dissolves perfectly in ether. The ethereal solution mixed with $\frac{1}{10}$th of alcohol, deposits no crystals on spontaneous evaporation,

excepting a little admixed cinchonine, and after incomplete neutrali-
sation with sulphuric acid, dries up to an amorphous yellow gum,
which may be triturated to a nearly white powder, dissolves easily in
all proportions of cold water, and when dried over the water-bath, con-
tains 10·65 p. c. of sulphuric acid.    On dropping alcoholic sulphuric
acid into an ethereal solution of amorphous quinine, the sulphate is
thrown down in the form of a yellow syrup.    The hydrochlorate (and
acetate) also is uncrystallisable : it is not affected by hyposulphite of
soda, but is precipitated in loose flocks by chloride of mercury
(Winckler).

Batka (*Chem. Centr.*, 1859, 913 ; *Pharm. Viertelj.* 9, 277) describes
as *quinio*, a yellow resin rich in quinine and resembling quinoïdine,
obtained by exhausting fresh cinchona-bark with alcohol and lime. He
supposes it to be the form in which cinchona-bases are present in the
bark.

*Conjugated Compounds of Quinine or Quinidine, and Compounds derived
therefrom.*

## Hydroquinine.

$$C^{46}N^2H^{26}O^6 = C^{40}N^2H^{24}O^6, H^2.$$
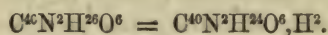
SCHÜTZENBERGER.    *Compt. rend.*, 46, 1065 ; *J. pr. Chem.* 74, 227
    *Ann. Pharm.* 108, 347 ; *Chem. Centr.* 1858, 541 ; *Kopp's Jahresber.*
    1858, 370.

*Hydrate de quinine.*  Contains H²O² more than quinine.

Obtained from quinine by the action of zinc and sulphuric acid in
the same manner as hydrocinchonine (p. 231).

Amorphous resin, nearly as bitter as quinine.    Softens at 35°, and
melts at 100° (as hydrated hydroquinine? Kr.). — Hydroquinine, dried
at 120°, contains 2 at. of water, one of which is expelled slowly at
140°, and the other at 150°.

Hydroquinine exhibits the same green coloration as quinine with
*chlorine-water* and *ammonia.*

It combines with 1 and 2 at. water.    (See above.)

|  |  | at 140°. |  |  | Schützenberger. |
|---|---|---|---|---|---|
| 40 C | ............ | 240 | ........ | 68·37 | ........ 68·40 |
| 2 N | ............ | 28 | ........ | 7·98 | |
| 27 H | ............ | 27 | ........ | 7·69 | ........ 7·53 |
| 7 O | ............ | 56 | ........ | 15·96 | |
| C⁴⁰N²H²⁶O⁶ + HO | .... | 351 | ........ | 100·00 | |

|  |  | at 120°. |  |  | Schützenberger. |
|---|---|---|---|---|---|
| 40 C | ............ | 240 | ........ | 66·66 | ........ 66·19 |
| 2 N | ............ | 28 | ........ | 7·78 | |
| 28 H | ............ | 28 | ........ | 7·78 | ........ 7·93 |
| 8 O | ............ | 64 | ........ | 17·78 | |
| C⁴⁰N²H²⁶O⁶ + 2HO | .... | 360 | ........ | 100·00 | |
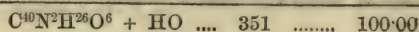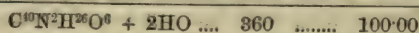
The salts of hydroquinine are more soluble than the corresponding

quinine-salts. The sulphate crystallises with difficulty. The *platinum-salt* contains, at 100°, 26·2 p.c. of platinum ($C^{40}N^2H^{26}O^6,2HCl, 2PtCl^2 = 26\cdot2$ p.c. Pt).

Hydroquinine dissolves in *alcohol* and in *ether*.

## Oxyquinine.

$$C^{40}N^2H^{24}O^6 = C^{40}N^2H^{22}O^6,H^2.$$
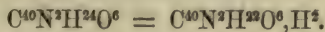
SCHÜTZENBERGER. *Compt. rend.* 47, 81; *J. pr. Chem.* 75, 124; *Ann. Pharm.* 108, 350; *Chem. Centr.* 1858, 678; *Kopp's Jahresber.* 1858, 371.

Sulphate of quinine is boiled with aqueous nitrite of potassium, and after the evolution of nitrogen has ceased, the cooled solution is precipitated by ammonia. The white crystalline precipitate is obtained in the anhydrous state by dissolving it in alcohol, evaporating the solution over the water-bath, and drying the residual resin at 130°.

Colourless, transparent resin, which does not melt at 140°. Less bitter than quinine.

| | | *at* 150°. | | | Schützenberger. |
|---|---|---|---|---|---|
| 40 C | ...... | 240 | ........ | 70·59 | 70·32 |
| 2 N | ...... | 28 | ........ | 8·23 | 6·36 (?) |
| 24 H | ...... | 24 | ........ | 7·06 | 7·40 |
| 6 O | ...... | 48 | ........ | 14·12 | 15·92 |
| $C^{40}N^2H^{24}O^6$ | ........ | 340 | ........ | 100·00 | 100·00 |

Oxyquinine in contact with *water* takes up a large quantity thereof and becomes converted into crystalline granules, which melt at 100°. It dissolves slightly in water.

The *platinum-salt*, $C^{40}N^2H^{24}O^6,2HCl,2PtCl^2$, contains 25·90 p.c. of platinum (by calc. 25·95 p.c. Pt).

Oxyquinine is soluble in *alcohol* and in *ether*.

## Quinine-sulphuric Acid.

$$C^{40}N^2H^{24}SO^7 = C^{40}N^2H^{24}O^4,SO^3.$$
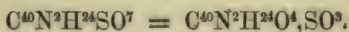
SCHÜTZENBERGER. *Compt. rend.* 47, 236.

*Acide sulfoquinique.*

Obtained by dissolving quinine in fuming sulphuric acid, in the same manner as cinchonine-sulphuric acid (p. 232), and resembles the latter body.

The baryta-salt yields, after drying at 100, 27·02 p.c. sulphate of baryta (calculation for $C^{40}N^2H^{23}BaO^4,SO^3$ requires 26·99 BaO,SO³). Has a bitter taste.

## Methyl-quinine.

$$C^{42}N^2H^{26}O^4 = C^{40}N^2H^{21}(C^2H^3)O^4,H^2.$$
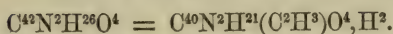
AD. STRECKER. *Ann. Pharm.* 91, 164.

The addition of 1 at. H. forms the hypothetical *methyl-quinium*, corresponding to ammonium. Known only in combination with hydriodic acid.

When iodide of methyl is added to an ethereal solution of quinine, crystals of hydriodate of methyl-quinine are formed in the liquid after standing for a while. The compound resembles hydriodate of ethyl-quinine in its behaviour with ammonia and caustic potash.

|  |  | at 100°. |  |  |  | Strecker. |
|---|---|---|---|---|---|---|
| 40 C | ............................... | 252 | ........ | 54·08 | ........ | 54·2 |
| 2 N | ............................... | 28 | ........ | 6·01 | | |
| 27 H | ............................... | 27 | ........ | 5·79 | ........ | 5·9 |
| 4 O | ............................... | 32 | ........ | 6·87 | | |
| I | ............................... | 127 | ........ | 27·25 | ........ | 26·9 |
| $C^{40}N^2H^{23}(C^2H^3)O^4,HI$ .... | | 466 | ........ | 100·00 | | |

## Ethyl-quinine.

$$C^{44}N^2H^{28}O^4 = C^{40}N^2H^{21}(C^4H^5)O^4,H^2.$$
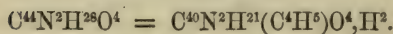
AD. STRECKER. *Ann. Pharm.* 91, 163.

With the addition of 1 at. H. it forms the *ethyl-quinium* of the ammonium-theory. Known only as hydrate, and in combination with acids.

Iodide of ethyl in contact with alcoholic or ethereal solution of quinine, forms, after some hours, yellow needles of hydriodate of ethyl-quinine, an aqueous solution of which is converted by oxide of silver into iodide of silver and a strongly alkaline solution of ethyl-quinine. When the latter is evaporated, and the amorphous residue is dissolved in alcohol and mixed with ether, a syrup is precipitated which is gradually converted into colourless needles, probably of *hydrate of ethyl-quinine.*

Tastes caustic and bitter in aqueous solution. — When heated to 120°, it evolves an odour of chinoline and decomposes. A strong alcoholic solution is not altered by iodide of ethyl.

Ethyl-quinine dissolves easily in *water.* It forms with *acids,* mono- and bi-acid salts. Aqueous ethyl-quinine absorbs carbonic acid from the air, and is converted into an uncrystallisable alkaline salt.

*Sulphate of Ethyl-quinine.* — A. *Mono-acid.* — Obtained by decomposing hydriodate of ethyl-quinine with sulphate of silver. Crystals which give off 14·8 p. c. of water at 110° (8 at. = 15·2 p. c. HO). Dissolves slightly in water, and more easily than B in alcohol.

| | Dried. | | | Strecker. |
|---|---|---|---|---|
| $C^{44}N^2H^{28}O^4$ ............... | 352 | ........ | 87·78 | |
| HO ........................... | 9 | ........ | 2·24 | |
| $SO^3$ ........................... | 40 | ........ | 9·98 | ........ 10·1 |
| $C^{44}N^2H^{28}O^4,HO,SO^3$.... | 401 | ........ | 100·00 | |

B. *Bi-acid.* — Aqueous ethyl-quinine mixed with a quantity of sulphuric acid sufficient to produce a strong acid reaction, leaves on evaporation a syrup, which, in contact with absolute alcohol, is transformed into crystals, which may be freed from excess of acid by washing with alcohol. — Needles, having an acid reaction, and losing 8·2 p. c. of water at 120° after drying over oil of vitriol (4 at. = 4 p. c. HO). — Dissolves very easily in water, without crystallising on evaporation; caustic potash throws down from the concentrated solution a precipitate soluble in water (probably mono-acid sulphate). The salt dissolves in alcohol.

| | Dried. | | | Strecker. |
|---|---|---|---|---|
| $C^{44}N^2H^{28}O^4$ .................... | 352 | ........ | 78·22 | |
| 2 HO............................... | 18 | ........ | 4·00 | |
| 2 $SO^3$............................... | 80 | ........ | 17·78 | ........ 18·2 |
| $C^{44}N^2H^{28}O^4,2HO,2SO^3$.... | 450 | ........ | 100·00 | |

*Hydriodate of Ethyl-quinine.* — Purified by washing with water and recrystallising from ether. — Very light, colourless, silky needles, neutral, unchangeable at 110°, melting at a higher temperature, without loss of weight, and solidifying to a vitreous mass on cooling. Tastes very bitter. Dissolves freely in water and is not precipitated by ammonia, but is thrown down in an unaltered state by a large quantity of caustic potash after standing for some time. Dissolves in alcohol, but not in ether.

| | at 100°. | | | Strecker. mean. |
|---|---|---|---|---|
| 44 C ........................ | 264 | ........ | 55·00 | ........ 54·9 |
| 2 N ........................ | 28 | ........ | 5·83 | |
| 29 H ........................ | 29 | ........ | 6·04 | ........ 6·2 |
| 4 O........................ | 32 | ........ | 6·66 | |
| I ........................ | 127 | ........ | 26·47 | ........ 26·4 |
| $C^{44}N^2H^{28}O^4,HI$ .... | 480 | ........ | 100·00 | |

*Hydrochlorate of Ethyl-quinine.* Obtained with difficulty from hydrochloric acid and ethyl-quinine, or more easily by decomposing nitrate of ethyl-quinine with chloride of sodium. — Slender needles, united in hemispherical groups. Neutral. Dissolves much more easily in boiling than in cold water.

| | at 120°. | | | Strecker. |
|---|---|---|---|---|
| $C^{44}N^2H^{29}O^4$............ | 353 | ........ | 90·86 | |
| Cl............................ | 35·3 | ........ | 9·14 | ........ 9·1 |
| $C^{44}N^2H^{28}O^4,HCl$.... | 388·5 | ........ | 100·00 | |

*Nitrate of Ethyl-quinine* does not crystallise on evaporation.

*Chloroplatinate of Ethyl-quinine.* — Yellow precipitate, crystallising from a solution in boiling water, on cooling, in indistinct crystals.

| | at 110°. | | | Strecker. |
|---|---|---|---|---|
| $C^{44}N^2H^{28}O^4,2HCl,4Cl$ ......., | 567·0 | ........ | 74·18 | |
| 2 Pt ................................. | 197·4 | ........ | 25·82 | ........ 25·4 |
| $C^{44}N^2H^{28}O^4,2HCl,2PtCl^2$.... | 764·4 | ........ | 100·00 | |

Hydrate of ethyl-quinine dissolves easily in *alcohol*.

## Ethyl-quinidine.

$$C^{44}N^2H^{28}O^4 = C^{40}N^2H^{21}(C^4H^5)O^4,H^2.$$
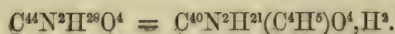
STENHOUSE.    *Ann. Pharm.* 129, 20,

Known only in combination with water and with acids.

Obtained as hydriodate of ethyl-quinidine by heating quinidine for half an hour with excess of iodide of ethyl. On separating the iodine from a solution of this salt by means of oxide of silver, the filtrate contains aqueous ethyl-quinidine, the alkaline bitter solution of which absorbs carbonic acid on evaporation, but yields no crystals.

*Sulphate of Iodethyl-quinidine* is obtained in the same way as the corresponding quinine-compound (Herapath).

*Hydriodate of Ethyl-quinidine.* — This salt alone, and not a compound of biethyl-quinidine, is obtained by again treating a strong aqueous solution of ethyl-quinidine with iodide of ethyl. — Long, silky needles, nearly insoluble in cold water, crystallising from boiling dilute alcohol.

| | at 100°. | | | Stenhouse. |
|---|---|---|---|---|
| $C^{44}N^2H^{29}O^4$ ..................... | 353 | ........ | 73·54 | |
| I ....................................... | 127 | ........ | 26·46 | ........ 26·39 |
| $C^{44}N^2H^{29}(C^4H^5)O^4,HI$ .... | 480 | ........ | 100·00 | |

*Chloroplatinate of Ethyl-quinidine.* — The hydriodate is decomposed by chloride of silver, and the filtrate precipitated by bichloride of platinum. — Pale-yellow powder. Dissolves very slightly in cold or boiling water, and somewhat more freely in hot dilute hydrochloric acid.

| | at 100°. | | | Stenhouse. |
|---|---|---|---|---|
| $C^{44}N^2H^{28}O^4$ ....................................... | 352 | ......... | 46·02 | |
| 2 HCl,4Cl ....................................... | 215 | ........ | 28·12 | |
| 2 Pt............................................... | 197·4 | ......... | 25·86 | ........ 25·61 |
| $C^{40}N^2H^{28}(C^4H^5)O^4,2HCl,2PtCl^2$ .... | 764·4 | ........ | 100·00 | |

## Benzoyl-quinine.

$$C^{54}N^2H^{28}O^6 = C^{40}N^2H^{23}(C^{14}H^5O^2)O^4.$$
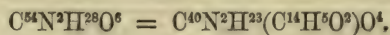
SCHÜTZENBERGER.    *Compt. rend.* 47, 234.

Chloride of benzoyl is poured upon quinine dried at 130°, whereupon an evolution of heat occurs, and the quinine deliquesces to a

thick syrup, composed of hydrochlorate of benzoyl-quinine and excess of chloride of benzoyl. The syrup is dissolved in water; the base is precipitated by ammonia; and the white resinous mass is dried at 140°, at which temperature it gives off a large quantity of water.

|  |  | at 140°. |  |  | Schützenberger. |
|---|---|---|---|---|---|
| 54 C | ............................... | 324 | ........ | 75·70 | ........ 75·76 |
| 2 N | ............................... | 28 | ........ | 6·54 |  |
| 28 H | ............................... | 28 | ........ | 6·54 | ........ 6·76 |
| 6 O | ............................... | 48 | ........ | 11·22 |  |
| $C^{40}N^2H^{23}(C^{14}H^5O^2)O^4$ | .... | 428 | ........ | 100·00 |  |

Benzoyl-quinine is coloured green by *chlorine-water* and *ammonia.* — The *platinum-salt* contains 23·2 p. c. platinum (calc. for $C^{40}N^2H^{23}(C^{14}H^5O^2)O^4$, $2HCl,2PtCl^2$ requires 23·5 p. c. Pt).

# Compounds of the Cinchona-bases with Iodine and Sulphuric Acid.

HERAPATH. 1. *Phil. Mag.* [4] 3, 161; 4, 186; *Chem. Soc. Qu. J.* 5, 177; abstr. with remarks by Zamminer; *Ann. Pharm.* 84, 149; *Kopp's Jahresber.* 1852, 148. — 2. *Phil. Mag.* [4] 6, 346; *Ann. Pharm.* 88, 207; *J. pr. Chem.* 61, 82; *N. Ann. Chim. Phys.* 40, 249. — 3. *Phil. Mag.* [4] 6, 171; *J. pr. Chem.* 61, 87; 2 and 3 in abstract; *Kopp's Jahresber.* 1853, 198. — 4. *Phil. Mag.* [4] 7, 352; *Dingl.* 134, 370; *J. pr. Chem.* 62, 367; *Kopp's Jahresber.* 1854, 156. — 5. *Phil. Mag.* [4] 9, 366; *J. pr. Chem.* 65, 380; *Kopp's Jahresber.* 1855, 150. — 6. *Phil. Mag.* [4] 14, 224; *J. pr. Chem.* 72, 104; *Kopp's Jahresber.* 1857, 405.—7. *Chem. Gaz.* 1858, 56; *J. pr. Chem.* 74, 415.—8. *Chem. Gaz.* 1858, 70; *J. pr. Chem.* 74, 411; Complete: *Chem. Soc. Qu. J.* 11, 130.—9. *Chem. Gaz.* 1858, 437; abstr. *J. pr. Chem.* 76, 364; *Rép. Chim. pure* 1, 39; 7 to 9; abstr. *Kopp's Jahresber.* 1858, 364.
HAIDINGER & STOKES. *Wien. Acad. Ber.* 10, 106; *Pogg.* 89, 250; *Kopp's Jahresber.* 1853, 198.

When the bi-acid sulphate of a cinchona-base is dissolved in a warm mixture of alcohol and acetic acid, or in dilute sulphuric acid, and mixed with a warm alcoholic solution of iodine, crystals separate on cooling, and are to be washed with alcohol and water, and dried at 93°.

The crystals contain, in all cases, iodine, sulphuric acid, and the base. They exhibit various colours of body and surface. Even in extremely thin plates they polarise light very completely, and possess also, in other respects, the optical properties of the tourmaline or Nichol's prism, for which they may be used as substitutes.

A solution of the crystals colours starch blue. It precipitates nitrate of silver, forming iodide of silver and a compound which is soluble only in strong nitric acid. The crystals, when treated with nitric acid, evolve iodine-vapour and nitric oxide; they dissolve quickly in oil of vitriol, turn red in cold strong hydrochloric acid, and form with the boiling acid a yellow solution, from which dull

yellow needles are deposited.  An alcoholic solution of the crystals is immediately decolorised by hydrosulphuric acid, soluble sulphides, sulphurous acid, and chlorine-water : from the solution treated with hydrosulphate of ammonia, or sulphide of potassium, alkalis precipitate the cinchona-base.  Aqueous alkalis and alkaline earths abstract the sulphuric acid, and leave a yellow residue containing iodine and the base.  The crystals dissolve in ammonia.

The crystals are nearly insoluble in water, but dissolve slightly in cold dilute acids and in weak alcohol.  They dissolve with brown colour in boiling alcohol, from which they crystallise on cooling ; water throws down from the solution a brown, amorphous precipitate. The crystals are nearly insoluble in ether and in chloroform.

If a solution contains at the same time quinine, quinidine, cinchonine, and cinchonidine, as bi-acid salts, tincture of iodine throws down first the quinine-salt, then a mixture of cinchonidine- and quinine-salts, and afterwards quinidine-salt, whilst the more soluble cinchonine-salt crystallises only (mixed with quinidine-salt) when a large quantity of cinchonine is present.  Thus the presence of cinchonidine in cinchonine, or of quinidine in quinine may be easily recognised.

1.  *Sulphate of Iodoquinine.* — *Herapathite* in the more restricted sense. 100 grammes of bi-acid sulphate of quinine, 1,440 grammes of acetic acid, and 120 grammes of dilute sulphuric acid (containing 10 per cent. of anhydrous acid) are heated to 100°, and a solution of 30 grammes of iodine in 1,150 grammes of alcohol is added, whereupon, after prolonged cooling to 4·5°, the mixture deposits an abundance of crystals, which are to be washed with acetic acid at 4·5°, re-crystallised repeatedly from boiling alcohol of sp. gr. 0·838, washed with cold alcohol, and dried at 32°, and at last over oil of vitriol.  Subsequently Herapath recommended 100 grammes of bisulphate of quinine, 1,920 grammes of acetic acid of sp. gr. 1·042, 480 grammes of alcohol of sp. gr. 0·837, and 60 grammes of alcoholic solution of iodine.  On the preparation of larger crystals for optical purposes see Herapath (2 and 4).  Elongated, rectangular, quadratic, octagonal, and rhombic laminæ, stellate groups of needles, or large, very thin plates.  By reflected light they exhibit a shining, cantharides-green colour, with metallic lustre ; by transmitted light they appear very pale olive-green or colourless, and perfectly transparent. The alcoholic solution is orange-coloured. When polarised at right angles to the axis the laminæ appear red, brown-red, or black.  Sp. gr. = 1·895 at 15°. — The salt dissolves in 1,000 parts of boiling water; in 650 parts of boiling alcohol of sp. gr. 0·837 at 13·9° ; in 50 parts of boiling alcohol.  Dissolves in 750 parts of acetic acid of sp. gr. 1·042 at 15·5°, and in 60 parts at the boiling heat ; on prolonged boiling iodine is evolved.

The crystals [dried over oil of vitriol (Hauers)] lose 2·49 p. c. (Herapath), 2·27 to 2·48 p. c. of water at 100° (Hauers).  No iodine is expelled in drying, but the crystals assume a brownish-red colour, and turn green again only on absorption of water (3 at. = 2·24 p.c. HO) (Hauers).

|  | at 100°. | | | | Herapath. |
|---|---|---|---|---|---|
| 80 C | 480 | ........ | 40·81 | ........ | 41·35 |
| 4 N | 56 | ........ | 4·76 | ........ | 3·54 |
| 51 H | 51 | ........ | 4·34 | ........ | 4·70 |
| 11 O | 88 | ........ | 7·48 | ........ | 9·81 |
| 3 SO³ | 120 | ........ | 10·19 | ........ | 9·77 |
| 3 I | 381·3 | ........ | 32·42 | ........ | 30·83 |
| 2 C⁴⁰N²H²⁴O⁴,3(HO,SO³),3I .... | 1176·3 | ........ | 100·00 | ........ | 100·00 |

|  | Over oil of vitriol. | | | | Hauers. |
|---|---|---|---|---|---|
| 80 C | 480 | ........ | 39·89 | ........ | 39·39 |
| 4 N | 56 | ........ | 4·64 | | |
| 54 H | 54 | ........ | 4·48 | ........ | 4·67 |
| 14 O | 112 | ........ | 9·36 | | |
| 3 SO³ | 120 | ........ | 9·96 | ........ | 9·98 |
| 3 I | 381·3 | ........ | 31·67 | ........ | 31·69 |
| 2 C⁴⁰N²H²⁴O⁴,3(HO,SO³),3I + 3 aq. ........ | 1203·3 | ........ | 100·00 | | |

Herapath gave the evidently incorrect formula $C^{57}N^2H^{33}O^5I^2,2(HO,SO^3) + 3$ aq. He formerly found 10·6 p. c. $SO^3$, 32·6 of iodine, 42·7 of quinine, and 14·1 of water. Hauers' analysis was made in Kraut's laboratory.

2. *Sulphate of Iodethylquinine.* — *Either* thin needles, perfectly opaque, *or* thick plates, transparent and purple-coloured in thin films, and of a shining metallic green colour by reflected light; *or* dark or orange-red laminæ, transparent and orange-yellow by transmitted light.

3. *Sulphate of Iodoquinidine.* — When a dilute solution of bi-acid sulphate of quinidine is heated to 70° or 80° with one-third or half its volume of alcohol, and a little tincture of iodine is added, long four-sided prisms of a deep garnet-red colour crystallise out. The crystals are purple-red by reflected, and dark brown-red by transmitted light. They dissolve in 121 parts of cold, and 31 parts of boiling alcohol, from which they are precipitated by water in the form of a cinnamon-brown powder. The crystals contain 32·76 p. c. C., 4·44 N., 3·98 H., 6·34 SO³, and 39·73 I, corresponding, according to Herapath, to the formula $C^{35}N^2H^{19}O^4I^2,SO^3,HO + 5$ aq. — Other and optically different crystals are obtained when tincture of iodine is dropped into a strong solution of bi-acid sulphate of quinidine mixed with 30 or 40 volumes of alcohol, at a temperature below 70° (Herapath) (9).

4. *Sulphate of Iodethylquinidine* is obtained in one form only, resembling the dark purple-red ethylquinine-salt.

5. *Sulphate of Iodoquinicine.* — Obtained in the preparation of 3, as a dark blood-red resin.

6. *Sulphate of Iodocinchonine.* — Long, four-sided, purple-black needles, deep purple-red by transmitted, dark purple-blue by reflected, light. Thin laminæ transmit lemon-yellow light. — Contains, on the average, 27·70 p. c. C., 3·31 N., 3·49 H., 50·41 I, and 5·23 SO³, and is, according to Herapath, $C^{35}N^2H^{19}O^2I^3,SO^3 + 6$ aq.

7. *Sulphate of Iodocinchonidine.* — Obtained in three different forms, with varying proportions of water. *a.* In green laminæ having a blue body-colour and a brass-yellow surface-colour. They contain, on the average, 35·49 p. c. C., 4·31 H., 8·63 SO³, and 39·22 O., corresponding,

according to Herapath, to the formula $C^{57}N^2H^{33}O^5I^3,2(SO^3,HO) + 5$ aq. These crystals absorb light as powerfully as the quinine-salt. — *b.* When *a* is allowed to remain long in the mother-liquor containing sulphuric acid, long golden-yellow, silky needles are formed; they contain 4 at. water more than *a*, and may be reconverted into *a* by crystallisation from alcohol. — *c.* The needles retain their yellow colour in the air, but become olive-green over oil of vitriol or at 100°, losing 5·32 p. c. (= 6 at.) of water. The olive-green salt is likewise converted into *a* by crystallisation from alcohol.

8. Wittstein's cinchonidine yields, with iodine and sulphuric acid, a salt having a deep bistre-brown body-colour, and a reddish-brown surface-colour. This salt differs from the foregoing.—(Herapath.)

## APPENDIX TO THE CINCHONA-BASES.

1. *Cinchona-yellow.* When the ethereal extract of cinchona-bark is exhausted with cold water, and the solution is evaporated, there remains a yellow extractive colouring matter, having a harsh taste, and forming with hydrate of alumina, a lake which is not affected by alcohol, but from which acids precipitate the colouring matter in a slightly reddened condition (Henry & Plisson, *J. Pharm.* 13, 371). The yellow is easily soluble in water and alcohol, and slightly soluble in ether. It is precipitated by basic acetate of lead, but not by tartar-emetic or tincture of galls (Pelletier & Caventou).

2. *Bitter Alkaloïd of Carapa-bark.* Extracted from the bark by boiling alcohol, after previous exhaustion with ether and cold alcohol. The red tincture is evaporated; the residue is exhausted with boiling water; the solution is boiled with magnesia; and the alkaloïd is extracted from the precipitate by boiling alcohol. — Yellowish, very bitter, alkaline mass, whose alcoholic solution is precipitated by tincture of galls and by oxalate of ammonia, the precipitate with the last reagent being soluble in acetic acid and easily in alcohol. — The acetate is not crystallisable (Petroz & Robinet, *J. Pharm.* 7, 349 ; *N. Tr.* 6, 2, 194).

3. *Copalche-bark*, which, according to Pereira, is obtained from *Croton Pseudochina*, contains a bitter organic base, soluble in ether, and precipitable from its salts by ammonia. It assumes a green colour with chlorine-water and ammonia, like quinine (Howard, *Pharm. J. Trans.* 14, 319 ; *Pharm. Viertelj.* 4, 458).

## Jamaïcine.

HÜTTENSCHMID. *Diss. sist. analys. Geoffroya jamaic. et surinam.* Heidelberg 1824 ; *Mag. Pharm.* 7, 287.
BUCHNER. *Repert.* 56, 164.
WINCKLER. *Jahrb. pr. Pharm.* 2, 162 ; *Pharm. Centr.* 1840, 120.
GASTELL. *Schweiz. Pharm. Wochenschr.* 1865, 97 ; *N. Repert.* 14, 211.

Discovered by Hüttenschmid in 1824, in the bark of *Geoffroya jamaïcensis.* It is identical with berberine (p. 185), as shown by Gastell, who examined jamaïcine prepared by Hüttenschmid himself.

*Preparation.* The bark is repeatedly boiled with alcohol; the filtrate is distilled to remove the greater part of the alcohol; the residue is dissolved in water; and the filtered solution is mixed with basic acetate of lead, and then treated with hydrosulphuric acid, without filtering, till the whole of the lead is precipitated. After filtering from sulphide of lead, the liquid is mixed with sulphuric acid, which throws down granules of sulphate of jamaïcine, more of which may be obtained by evaporating and cooling the remaining liquids. The sulphate is collected, pressed, and dissolved in water, and the solution is digested with carbonate of baryta, filtered, and evaporated to crystallisation (Hüttenschmid). — When the solution which has been freed from lead is evaporated to dryness, and the residue is exhausted with a little cold alcohol, acetate of jamaïcine remains undissolved, whilst a *yellow colouring matter* is taken up, though, according to Buchner, this latter is nothing but impure jamaïcine. — Buchner mixes the extract prepared with hot water, after drying and powdering, with freshly ignited charcoal, and extracts the jamaïcine from the mixture by repeated treatment with warm alcohol.

*Properties.* Pomegranate-yellow, semi-transparent quadratic tables, melting below 100° (Hüttenschmid). Yellowish-brown, crystalline powder, or yellow needles (Gastell). Inodorous and bitter. Neutral to vegetable colours. Not decolorised by charcoal.

When *heated* it melts to a brown-red liquid, swells up very much, and burns, giving off vapours which redden turmeric and smell of roasted cocoa.

According to Hüttenschmid, jamaïcine dissolves easily, according to Buchner, with difficulty, in *water.* The solution in 50 parts of water is of a fine yellow colour (Winckler). — *Potash* and *ammonia* colour the aqueous solution red-brown (Gastell).

The *salts of jamaïcine* are bitter, crystalline, soluble in water and alcohol, and are not decolorised by animal charcoal. Aqueous jamaïcine precipitates most metallic salts. — The *phosphate* forms lemon-yellow granules; the *sulphate* sulphur-yellow needles; also the *hydrochlorate*, which melts below 100°. The *nitrate* forms yellow crystalline crusts, which dissolve in water and alcohol and melt below 100°. — Aqueous jamaïcine is precipitated in the crystalline form by *oxalic* acid after some time, but not by *tartaric* acid (Hüttenschmid). — Jamaïcine exhibits the behaviour of berberine towards *iodide* and *biniodide of potassium, bichromate of potash, nitrate of silver, hyposulphite of soda and silver-oxide, chloride of gold,* and *cyanide of potassium:* mineral acids in excess also precipitate aqueous solutions of its salts. *Chloroplatinate of jamaïcine* is thrown down as a reddish-yellow gelatinous precipitate, which becomes flocculent on warming, and contains, at 100°, 17·75 p. c. of platinum (calc. for chloroplatinate of berberine requires 18·22 p. c. Pt.) (Gastell).

*Acetate of Jamaïcine.* — If the liquid obtained in the preparation of jamaïcine, after precipitating the lead by hydrosulphuric acid, be evaporated, without addition of sulphuric acid, the remaining granular extract, exhausted with a little cold alcohol, and the undissolved portion purified by recrystallisation from water, yellow, bitter, four-sided tables are obtained. These tables melt below 100°, evolve an odour

of acetic acid when treated with sulphuric acid, and dissolve easily in water, and less freely in alcohol (Hüttenschmid).

Jamaïcine dissolves in *alcohol*, but is nearly insoluble in *ether*. It is precipitated of a yellow colour by *tincture of galls*.

## 5. Surinamine.

Hüttenschmid. *Dissert.* Heidelberg, 1824.
Winckler. *Jahrb. pr. Pharm.* 2, 159.

*Geoffroyine.* An alkaloïd from the bark of *Geoffroya surinamensis.* Recognised also by Overdun in 1824. Erroneously regarded as alumina by van der Byll (*Mulder's Natuur-en Scheikund. Archief.* I, 295 ; abstr. *Ann. Pharm.* 7, 265).

*Preparation.* An alcoholic extract of the bark is exhausted with water ; the filtrate is precipitated by basic acetate of lead and again filtered ; and the liquid is freed from lead by hydrosulphuric acid, filtered, and evaporated, whereupon a portion of the surinamine is deposited. The remainder is obtained by digesting the liquid with magnesia, filtering, and evaporating further (Hüttenschmid). The surinamine thus separated is purified by washing with cold water and crystallising from boiling water. A pound of the bark yields 30 grains (Winckler).

*Properties.* White, very fine, bulky, woolly needles, having a faint taste. Without action on pigeons, in doses of two grains. Neutral to litmus and turmeric.

*Decompositions.* When carefully *heated*, a portion appears to volatilise unaltered, but the greater part blackens, evolves vapours smelling like melted quinine, and leaves a combustible charcoal (Winckler). — When heated in a glass vessel, it emits an odour of bruised plumkernels, and yields a liquid which reddens turmeric, and leaves charcoal (Hüttenschmid). With nitric acid containing nitrous acid, it yields first a violet, then a brilliant prussian-blue-coloured liquid (Hüttenschmid). Winckler obtained with strong nitric acid a colourless solution, which evolved nitrogen in abundance over the water-bath, and left a residue soluble in water with yellow colour. — *Oil of vitriol* dissolves surinamine, forming a colourless liquid, which turns brown when heated (Winckler).

Surinamine dissolves very slightly in cold, but easily in boiling *water :* the solution is not affected by iodine, ammonia, mercurous nitrate, or tincture of galls (Hüttenschmid ; Winckler).

Surinamine dissolves very easily in dilute *sulphuric* and *hydrochloric acids.* The solution in sulphuric acid yields crystalline laminæ on evaporation, the solution in hydrochloric acid, white needles, which turn white and opaque in water (Hüttenschmid). By evaporating the hydrochloric acid solution over the water-bath, Winckler obtained a colourless transparent residue, which reddened litmus, precipitated silver-salts, and turned milk-white when digested in water.

Surinamine dissolves in *caustic potash* more freely than in water : on

evaporating the solution a white pellicle, made up of nodules, remains (Hüttenschmid).

Surinamine is nearly insoluble in cold, slightly soluble in boiling *alcohol*, and insoluble in *ether*.

## 6. Pereirine.

Goos. *Repert.* 76, 32; *Pharm. Centr.* 1839, 610; *Berz. Jahresber.* 23, 372.
PERETTI. *J. Chem. méd.* 26, 162.

An alkaloïd contained in *Cortex Pereiræ* from Brazil, which is probably obtained from a species of *Cerbera* (*Handbuch*, viii [2], 57). First prepared by Blank in Rio Janeiro, then by Dos Santos, and lastly by Goos.

*Preparation.* The bark is exhausted with acidulated water, and the extract precipitated by aqueous ammonia. From the precipitate thus obtained, the pereirine is extracted by ether, which leaves it on evaporation, and the residue is purified by solution in dilute hydrochloric acid and precipitation by ammonia (Goos). Yellow, but not colourless, pereirine is obtained also by decomposing the platinum-salt with hydrosulphuric acid, and precipitating the acid solution with ammonia (Berzelius).

*Properties.* Whitish-yellow, amorphous, very bitter powder. According to Peretti, it may be obtained from alcohol or ether in granules. Has an alkaline reaction.

Pereirine melts, when *heated*, without loss of water, to a blood-red mass, emitting an odour of melted quinine, and afterwards puffs up, blackens, and leaves a porous charcoal. — When submitted to dry distillation, it evolves ammonia. — Dissolves in strong *nitric acid*, with fine purple-red colour (Pelletier, *J. Pharm.* 26, 162), with blood-red colour, which changes to greyish-brown and disappears on diluting the solution (Goos). A solution of sulphate of pereirine, reddened by nitric acid, is not precipitated by ammonia or potash; on evaporating the solution, bitter white granules and needles are obtained, which are again reddened by nitric acid (Peretti). — *Oil of vitriol* dissolves pereirine, with fine violet colour, changing to brown, and on dilution with water to olive-green, and lastly to grass-green.

Pereirine dissolves very slightly in *water*, to which it imparts its bitter taste. — It combines with *acids* to form neutral, amorphous salts, which are for the most part soluble in water and alcohol. The solution in dilute *sulphuric acid* yields indistinct crystalline granules on evaporation (Peretti). — Aqueous solutions of pereirine-salts are precipitated yellowish-white and pulverulent by *oxalate of potash*, but not by free oxalic acid. — *Hydrochlorate of pereirine* produces with *bichloride of platinum* a yellow precipitate, but slightly soluble in water (Berzelius).

Pereirine dissolves in *alcohol* and *ether*.

7. *Pitoyine.* — Occurs, according to Peretti (*N. J. Pharm.* 21, 515), in *China bicolor* (*Wigg.* 429), which was examined by Peretti as *China*

*pitoya.* — An aqueous extract of the bark is treated with alcohol of 34°; the tincture is diluted and distilled, and the aqueous residue precipitated by ammonia. The precipitate is treated with ether, which takes up tannate of pitoyine, and leaves a residue soluble in boiling water. This solution is mixed with sulphuric acid and purified by animal charcoal; the excess of acid is removed by means of lime; and the solution is evaporated. On dissolving the residue in alcohol, and evaporating the filtrate, fan-shaped crystals of sulphate of pitoyine remain. — Pitoyine tastes bitter in solution, though not in the solid state. It melts above 100°, giving off very bitter vapours, which sublime in needles, and afterwards empyreumatic products. It is decomposed by boiling nitric acid. Forms with sulphuric acid a crystallisable, and with acetic acid an uncrystallisable salt. Dissolves in water and alcohol, and very easily in ether.

Since Peretti's bark contained, according to Guibourt (*Hist. des drogues*, 3, 141), a large quantity of quinine and cinchonine, his pitoyine cannot be regarded as a distinct substance (Gerhardt, *Traité*, 4, 105).

## Primary Nucleus C⁴⁰H³⁰.

## Sylvic Acid.

$$C^{40}H^{30}O^4 = C^{40}H^{30},O^4.$$
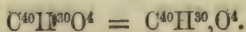
UNVERDORBEN. *N. Tr.* 8, 1, 21; abstr. *Pogg.* 7, 311.—*Pogg.* 8, 40, and 407; 11, 28, 230, and 393; 14, 116; 17, 186.
TROMMSDORFF. *Ann. Pharm.* 13, 169.
ROSE. *Pogg.* 33, 42; *Ann. Pharm.* 13, 184. — *Pogg.* 53, 374.
LAURENT. *Ann. Chim. Phys.* 65, 324; 68, 395; 72, 459: *Ann. Pharm.* 34, 272. — *N. Ann. Chim. Phys.* 22, 459; *J. pr. Chem.* 45, 61.
SIEVERT. *Zeitschr. für d. ges. Naturwissenschaften,* 14, 311: *Kopp's Jahresber.* 1859, 508.
MALY. *Wien. Acad. Ber.* 44, 121; *Krit. Zeitschr.* 5, 47; *Kopp's Jahresber.* 1861, 389.

Discovered and investigated by Unverdorben, but confounded by him and all later investigators except Maly, with abietic acid, the acid existing ready formed in pine-resin. Owing to this confusion, it is not always clear which statements refer to abietic and which to sylvic acid. Unverdorben, however, seems to have examined principally an acid prepared with sulphuric acid — therefore sylvic acid. Laurent's statements apply better to sylvic acid, though his method of preparation must have yielded abietic acid (Kr.).

Two acids found by Baup (*Ann. Chim. Phys.* 31, 108) in French colophony, *acide pinique* and *acide abiétique*, as well as Lecanu & Bussy's *crystallised acid from turpentine* (*J. Pharm.* 13, 62) appear to belong to this head.

*Formation and Preparation.* — 1. *From Abietic acid.* An alcoholic solution of abietic acid is precipitated by dilute sulphuric acid, and the hardened crystalline precipitate is washed with alcohol, and afterwards crystallised from that liquid (Maly). — Sylvic acid is obtained also, together with sylvinolic acid, by passing hydrochloric acid gas into a solution of abietic acid in alcohol (Maly).

$$C^{88}H^{64}O^{10} + 2HO = C^{40}H^{30}O^4 + C^{48}H^{34}O^6 \text{ (Kr.)}.$$
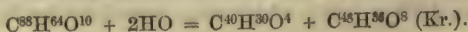
2. *From White Pitch, Colophony, &c.* — White pitch is allowed to stand, covered with an equal quantity of alcohol, till it is completely saturated with the liquid, and until the turpentine-like deposit formed at first has become crystalline. It is collected on a cloth, triturated with a little alcohol, washed with that liquid on the filter, and afterwards dissolved in a small quantity of hot absolute alcohol containing sulphuric acid : the solution cools to a crystalline mass. Purification is effected by pressing the crystals, and repeatedly subjecting a hot alcoholic solution to fractional precipitation with hot water, whereby the less pure portions are thrown down first. The alcoholic solution, mixed with a quantity of hot water barely sufficient to produce turbidity, yields large crystals on cooling (Trommsdorff).

Ries had previously observed that acids produce large crystals in the alcoholic solution of white pitch. Unverdorben purified his sylvic acid by dissolving it in 2 parts of absolute alcohol containing $\frac{1}{16}$th of oil of vitriol : Sievert proceeded in a similar manner. Rose and Liebig obtained their acid from Trommsdorff.

Laurent boils pine-resin with water to free it from turpentine ; extracts the pinic acid by means of cold alcohol, and dissolves the residue in boiling alcohol. The solution on cooling yields crystals, which are freed from adhering oil by washing with cold alcohol, and recrystallisation from boiling alcohol. Unverdorben, and likewise Trommsdorff and Sievert, employ similar methods. The product thus obtained is abietic acid (Maly).

Long standing of the alcoholic solution reduces the yield of the crystals (Sievert).

*Properties.* Colourless, transparent, tabular, rhomboïdal prisms, with four-sided summits (Unverdorben); indistinctly crystalline masses, also triangular laminæ (Rose ; Laurent). Right prismatic ? According to Sievert, they are doubly oblique prismatic (triclinic). The crystals exhibit the faces *u*, *t*, and *a* (Fig. 66), but with peculiar hemimorphous development. Of the octahedron *a* in particular, only the upper left posterior, and the lower right posterior are developed, so that the left half of the prism disappears, and the face appears in the form of a triangle. Anterior *u* : posterior $u = 96°$ ; $u : t = 132°$. The remaining upper octahedral face makes with the anterior face *t* an angle of $70°$ ; the lower octahedral face with the posterior *t*, an angle of $110°$. The plane angles of the triangular faces *t* are $90°$, $45°$, and $45°$. Vitreous, very brittle, triturable to a white powder (Sievert). — Does not lose weight at $100°$, or in a vacuum, and melts without loss of weight (Unverdorben) at $152·5°$, but becomes quite fluid at higher temperatures (Trommsdorff). In a warm tube the crystallised acid, as well as that which has been previously fused, melts at $162°$, but when heated in a retort it cakes together, partially at $118°$, and completely at $150°$, and melts to a thin, clear liquid, which turns thick at $120°$, viscid at $110°$, and solidifies to a glassy mass, afterwards melting partially at $135°$, and completely at $155°$ (Sievert). The lower melting-point of the previously melted amorphous acid had been previously observed by Wöhler, (*Ann. Pharm.* 41, 155.) — Sylvic acid sublimes partially at $170°$, in a thin crust, which, when dissolved in alcohol, yields crystals of the unchanged acid ; the residue turns dark-red at $240°$, but does not boil even at $290°$ (Sievert). Distils without much decomposition, yielding a trace of water, and a colophony-like distillate, an alcoholic solution of which yields crystals of unchanged sylvic acid, whilst the residue contains a trace of charcoal (Laurent). — Inodorous and tasteless ; reddens litmus. Rotates a ray of polarised light to the left, more powerfully than pimaric acid. Sp. gr. = $1·1011$ at $18°$ (Sievert).

| | | | | Tromms- dorff. | | Liebig. | | Rose. earlier. | | later. |
|---|---|---|---|---|---|---|---|---|---|---|
| 40 C | ........ | 240 | .... | 79·47 | .... | 78·90 | .... | 78·65 | .... | 78·07 | .... | 78·54 |
| 30 H | ........ | 30 | .... | 9·93 | .... | 9·82 | .... | 9·82 | .... | 9·93 | .... | 9·96 |
| 4 O | ........ | 32 | .... | 10·60 | .... | 11·28 | .... | 11·53 | .... | 12·00 | .... | 11·50 |
| $C^{40}H^{30}O^4$.... | | 302 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 |

| | Laurent. | Sievert. | Maly. |
|---|---|---|---|
| C ...................... | 77·39 | 79·14 | 79·12 |
| H ...................... | 9·90 | 9·75 | 10·08 |
| O ...................... | 12·71 | 11·11 | 10·80 |
| | 100·00 | 100·00 | 100·00 |

Abietic acid contains 78·57 p. c. C., and 9·52 H.

*Amorphous Sylvic acid?* Alcoholic sylvic acid becomes uncrystallisable on standing (Rose; Sievert); by spontaneous evaporation of the solution in a vacuum there is obtained a white, brittle mass which melts over the water-bath, losing 2 per cent. in weight, and then contains, on the average, 74·31 p. c. C., 8·83 H., and 16·86 O. On one occasion the amorphous mass had the composition of sylvic acid (Rose). See also Hesse (*Ann. Pharm.* 29, 141), who examined a similar product with 71·16 p. c. C. and 8·74 H. as *oxysylvic acid.*

*Decompositions.* 1. Sylvic acid submitted to *dry distillation* (see above) yields water and empyreumatic oil, then a little gas, followed first by a thinner and afterwards a thicker oil, containing sylvic and pinic acids and a large quantity of a neutral resin and oils. — 2. *Nitric acid* slowly decomposes sylvic acid, and dissolves it only on prolonged boiling; water throws down from the solution yellow flocks, soluble in ammonia, caustic potash, and alcohol. — 3. *Oil of vitriol* rapidly dissolves sylvic acid, forming a yellowish-brown solution, from which water precipitates unchanged sylvic acid and a large quantity of pinic acid (Unverdorben).

*Combinations.* Sylvic acid combines with *bases*, with elimination of water (Unverdorben; Laurent) (contrary to Rose). It expels the acid from carbonates, and when melted also from succinates and benzoates and from chloride of calcium; but salts of sylvic acid, dissolved in water, are decomposed by boric and acetic, and by stronger acids, with precipitation of sylvic acid. The salts are obtained—1. By dissolving the acid in the aqueous base. 2. By precipitating an acetate dissolved in alcohol by means of alcoholic sylvic acid, dissolving the precipitate in ether, and re-precipitating by alcohol, which retains in solution the excess of sylvic acid. — 3. By double decomposition. — Some of the sylvates are crystallisable; a few of them are soluble in water and alcohol, and all of them in ether (Unverdorben).

*Sylvate of Ammonia.* The easily formed syrupy solution of the acid in aqueous ammonia becomes turbid on evaporation, and deposits the acid when boiled. — The white semi-fluid precipitate thrown down by sal-ammoniac from sylvate of potash is, according to Unverdorben, monosylvate of ammonia, soluble in 200 parts of water.

*Sylvate of Potash.* — a. *Basic?* — Caustic potash dissolves sylvic acid precipitated by water, but the addition of more acid throws down a difficultly soluble salt (Rose). From sylvic acid dissolved in ether and carbonate of potash a colourless amorphous salt is obtained (Unverdorben). —

b. *Mono-acid.* When sylvic acid is boiled with 6 parts of alcohol and with carbonate of potash, the filtrate on cooling deposits delicate, white needles, which may also be obtained by mixing the salt *a* with alcoholic sylvic acid (Unverdorben; Sievert). Melts to a resin when heated; dissolves very slightly in water, slowly in 20 parts of alcohol, more freely in hot alcohol. Dissolves abundantly in warm ether and oil of turpentine, and to a less extent in olive-oil (Unverdorben).

|  | | Needles. | | | | Sievert. |
|---|---|---|---|---|---|---|
| 40 C | .................. | 240 | .......... | 70·55 | .......... | (69·67) |
| 29 H | .................. | 29 | .......... | 8·52 | .......... | 8·45 |
| 3 O | .................. | 24 | .......... | 7·05 | .......... | 8·29 |
| KO | .................. | 47·2 | .......... | 13·88 | .......... | 13·59 |
| $C^{40}H^{29}KO^4$ | ........ | 340·2 | .......... | 100·00 | .......... | 100·00 |

c. *Quadracid.* — Boiling alcoholic potash, neutralised with sylvic acid and cooled, solidifies to a crystalline mass, which may be purified by recrystallising and pressing. The same salt is precipitated from alcoholic sylvic acid by an alcoholic solution of acetate of potash. — Fine, silky tufts of delicate needles. Decomposes when boiled with water, ¾ths of the acid being precipitated, whilst the mono-acid salt remains in solution (Sievert).

|  | | Needles. | | | | Sievert. |
|---|---|---|---|---|---|---|
| 160 C | ............................... | 960 | ........ | 77·03 | ........ | 76·95 |
| 119 H | ............................... | 119 | ........ | 9·55 | ........ | 9·58 |
| 15 O | ............................... | 120 | ........ | 9·63 | ........ | 9·51 |
| KO | ............................... | 47·2 | ........ | 3·79 | ........ | 3·96 |
| $C^{40}H^{29}KO^4,3C^{40}H^{30}O^4$ | ........ | 1246·2 | ........ | 100·00 | ........ | 100·00 |

The *soda-salt* is obtained in crystals by boiling alcoholic sylvic acid with excess of carbonate of soda and cooling the filtrate (Unverdorben). — The *baryta-salt* dissolves in 3,000 parts of water, in 6 parts of cold, and less of boiling absolute alcohol, from which it is deposited in microscopic crystalline flocks on cooling (Unverdorben).

*Sylvate of Lime.* — The solution of the salt in cold absolute alcohol deposits colourless, shining, crystalline granules on spontaneous evaporation (Unverdorben). — The mono-acid salt is obtained by the double decomposition of sylvate of potash and chloride of calcium, and a salt containing a smaller proportion of lime, by precipitating alcoholic sylvic acid with an alcoholic solution of acetate of lime (Sievert).

|  | | | | | Sievert. |
|---|---|---|---|---|---|
| 40 C | .............. | 240 | ........ | 74·76 | 74·45 |
| 29 H | .............. | 29 | ........ | 9·03 | 8·78 |
| 3 O | .............. | 24 | ........ | 7·48 | 8·36 |
| CaO | .............. | 28 | ........ | 8·73 | 8·41 |
| $C^{40}H^{29}CaO^4$ | ........ | 321 | ........ | 100·00 | 100·00 |

*Sylvate of Magnesia* dissolves in all proportions in alcohol of 65 per cent. and in absolute alcohol; from the latter solution a double volume of water throws down a colourless semi-fluid salt, which dries up to a transparent resin in the air, and dissolves in ether and in rock-oil. — The sylvates of *manganese* and *zinc* are soluble in absolute alcohol.

*Sylvate of Lead.* — The acid loses 3·02 p. c. of water when heated to 168° with oxide of lead (1 at. = 2·97) (Sievert). The precipitate thrown down by an alcoholic solution of sylvic acid from alcoholic neutral acetate of lead is a white, amorphous powder, easily fusible, and containing, on an average, 26·94 p. c. of oxide of lead (1 at. = 26·17 p.c. PbO) (Rose).

The *ferrous* and *ferric salts* dissolve slightly in alcohol and easily in ether (Unverdorben).

*Sylvate of Copper.* — Dissolves in ether and crystallises from absolute alcohol in shining granules (Unverdorben). — *a.* Alcoholic sylvic acid is precipitated by an alcoholic solution of acetate of copper; the pale blue flocks thus obtained run together when warmed. The precipitate is powdered and repeatedly exhausted with alcohol. — From the filtrate from *a,* water throws down the pale blue precipitate *b.* — *c.* When a boiling alcoholic solution of sylvic acid is precipitated with alcoholic acetate of copper, aqueous ammonia added till the precipitate is dissolved, and the solution then cooled or mixed with water, a dark blue precipitate is produced, which is triturable to a pale blue powder after drying (Sievert). Trommsdorff drops alcoholic sylvic acid into excess of alcoholic acetate of copper, and washes the precipitate with water. The pale blue precipitate contains 11·38 p. c. of oxide of copper at 109°, and is, therefore, the mono-acid salt.

|  |  |  |  |  | *a.* | | Sievert. *b.* | | *c.* |
|---|---|---|---|---|---|---|---|---|---|
| 40 C | .......... | 240 | ........ | 72·14 | ........ | 71·52 | ........ | 67·66 | ........ | 71·64 |
| 29 H | .......... | 29 | ........ | 8·72 | ........ | 8·61 | ........ | 7·82 | ........ | 8·72 |
| 3 O | .......... | 24 | ........ | 7·21 | ........ | 9·37 | ........ | 8·81 | ........ | 7·38 |
| CuO | .......... | 39·8 | ........ | 11·93 | ........ | 10·50 | ........ | 15·71 | ........ | 12·26 |
| C⁴⁰H²⁹CuO⁴.... | | 332·8 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

*Sylvate of Silver.* — Crystallises from alcohol in shining granules on spontaneous evaporation. When boiled with potash and oil of turpentine, it behaves like pinate of silver. — Dissolves in 15 parts of cold, and in a smaller quantity of boiling alcohol, and instantaneously in ether, which takes it up from water when suspended therein (Unverdorben). — The precipitate produced by alcoholic nitrate of silver in alcoholic sylvic acid on addition of ammonia, contains 26·01 p. c. of silver (1 at. = 26·4 p. c. Ag.) (Rose). The silver-salt prepared with sylvic acid obtained by the first method (p. 318), contains 25·88 p. c. silver (Maly).

Sylvic acid dissolves in *acetic acid.* It dissolves very slightly in cold alcohol of 65 p. c., and in about 3 parts of the boiling liquid, from which it crystallises on cooling, about 1/25th only remaining in solution. It dissolves in about 3 parts of cold, and 1 part of boiling absolute alcohol or ether, and is thrown down from the former solution by an equal quantity of water, as a semi-transparent oil, which hardens to a crystalline solid on addition of more water, or on exposure to the air (Unverdorben). Sylvic acid dissolves in 10 parts of cold, and in 4/5ths of boiling alcohol of 92 p. c.; more freely, therefore, than pimaric acid (Sievert). — It dissolves in *acetic ether, rock-oil,* and *oil of turpentine,* without crystallising therefrom (Unverdorben).

## Pimaric Acid.

$$C^{40}H^{30}O^4 = C^{40}H^{30},O^4.$$
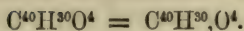
LAURENT.   *Ann. Chim. Phys.* 72, 384; *Ann. Pharm.* 34, 272. — *N. Ann.*
   *Chim. Phys.* 22, 459; *Compt. rend.* 21, 858; *J. pr. Chem.* 45, 61.
SIEVERT.   *Zeitschr. für die gesammt. Naturwissensch.* 14, 311.

Occurs in the turpentine of *Pinus maritima*, which hardens to *galipot* in the air,
and also in colophony from Bordeaux.  Compare p. 319, and *Abietic* acid.

*Preparation.*  Galipot, which occurs in commerce, mixed with tur-
pentine, is freed from the latter body, broken up, and digested with
a mixture of 1 part of ether and 6 parts of alcohol, which is poured off
after standing for a short time.  The undissolved portion is again
treated twice in the same way, and then dissolved in boiling alcohol :
on standing for some days the solution deposits crystalline crusts,
which are removed from time to time, and purified by recrystallisation
from boiling alcohol (Laurent).  Or, Bordeaux colophony is washed
with cold alcohol, and the residue is dissolved in boiling alcohol and
allowed to crystallise (Laurent).

*Properties.*  White, nodular crystalline crusts, consisting of micro-
scopic, rectangular, or sometimes six-sided prisms (Laurent).  Thin
laminæ, derived from a quadratic prism, often truncated at the edges or
acuminated (Sievert).  Melts about 125°, and solidifies only at 68° to a
transparent, or sometimes granulo-crystalline mass.  The acid dried
in a vacuum loses $\frac{4}{10}$ths p. c. of water when melted (Laurent).  Runs
together at 120° to 135°, and at 158° melts completely to a clear
liquid, from which some of the acid sublimes unchanged at 120°.  In
a narrow tube the crystallised acid, as well as that which has pre-
viously melted, melts at 155° (Sievert).  Sp. gr. 1·1047 at 18°.  Exerts
a left-handed action on polarised light, less powerful than sylvic acid
(Sievert).

|        |     |     |        | Laurent. | Sievert. |
|--------|-----|-----|--------|----------|----------|
| 40 C   | 240 | ... | 79·47  | 78·18    | 79·02    |
| 30 H   | 30  | ... | 9·94   | 9·74     | 9·87     |
| 4 O    | 32  | ... | 10·59  | 12·08    | 11·11    |
| $C^{40}H^{30}O^4$ | 302 | ... | 100·00 | 100·00 | 100·00 |

Isomeric with sylvic acid. — Maly is inclined to regard pimaric acid as abietic
acid, $C^{88}H^{64}O^{10}$, in which I agree with him (Kr.).

*Amorphous Pimaric acid.* — Crystallised pimaric acid becomes amorphous on
keeping.  White crystalline crusts of pimaric acid lost their transparency in three
months and became yellow and friable.  When dissolved in boiling alcohol, they
yielded, on cooling and evaporating, an amorphous syrup free from crystals.  The
acid thus altered dissolves in its own weight of alcohol, from which it does not
crystallise.  It is thrown down from the solution by water as a soft mass, but still
possesses the composition of the crystallised acid (78·45 p. c. C., 9·63 H., 11·92 O.).
This alteration does not occur with the fused acid, nor with that dissolved in alcohol
(Laurent).  Laurent afterwards regarded amorphous pimaric acid as identical with
pinic acid (see below).

*Decompositions.*  1. Pimaric acid assumes a yellow-brown colour on

prolonged *melting*. On *distilling* 10 grammes in a vacuum, there pass over first traces of water, and then a liquid, Laurent's *pyromaric acid* (p. 325), which solidifies, for the most part, in the neck of the retort, the contents of the retort remaining of a transparent yellow to near the end of the process, and leaving only a trace of charcoal. When the acid is distilled in larger quantity in vessels containing air, *pimarone* is also obtained (Laurent).

When the viscid distillate is saponified by caustic potash, the pimarone is taken up by the soap, and on drying and powdering the soap, and afterwards shaking it with ether, the pimarone is dissolved by that liquid, together with a little potash-salt, which is removed by water. The remaining pimarone is washed with aqueous potash and with water, and dried in a vacuum. Thus obtained it is yellowish, resembles a fatty oil, and is soluble in ether and alcohol. It hardens almost completely in the air. Contains 84·20 p. c. C., 10·32 H., and 5·48 O., corresponding to the formula $C^{40}H^{28}O^2$ (calc. = 84·5 C., 9·85 H.) (Laurent).

2. By the action of boiling *nitric acid* on pimaric acid, nitromaric acid is produced (Laurent). — 3. On adding powdered pimaric acid gradually to *oil of vitriol*, a brown-red solution is obtained, which, after standing for 24 hours, deposits grey flocks when poured into water. These flocks are rendered nearly colourless by washing with water; they do not crystallise from alcohol, and yield no pyromaric acid when submitted to dry distillation : they contain, at 100°, 76·69 p. c. C., 9·68 H., and 13·69 O. (Laurent).

*Combinations.* Pimaric acid is insoluble in *water*. It forms soluble salts with ammonia and the alkalis. Its alcoholic solution does not precipitate alcoholic solutions of chloride of barium (?), strontium, calcium, or magnesium, but on addition of ammonia an abundant white precipitate is produced in the lime-solution, whilst in the other solutions a smaller precipitate is formed, or precipitation takes place only on cooling ; the baryta solution does not yield any precipitate. An alcoholic solution of the acid, mixed boiling with alcoholic acetate of lead, copper, or silver, throws down amorphous salts after some time (Laurent).

*Lead-salt.* — The acid heated with oxide of lead loses 2·8 to 3·4 p. c. water (1 at. = 2·98 p. c. HO.). — The lead-salt obtained by precipitating boiling alcoholic neutral acetate of lead with the alcoholic acid, contains, after drying in a vacuum, 26·5 p. c. oxide of lead ($C^{40}H^{29}PbO^4$ = 27·65 p. c. PbO.). — This white lead-salt, when heated, melts to a resin, cooling to a yellow transparent mass, which, when subjected to dry distillation, yields water and a thick oil soluble in caustic potash, and leaves charcoal and lead (Laurent).

Pimaric acid dissolves in 10 parts of *alcohol* at 18°, and in its own weight of boiling alcohol ; it is precipitated from the solution by water in flocks which do not cake together (Laurent). The acid dissolves in 13 parts of alcohol of 92 p. c. (Richter); in 2 parts of boiling alcohol (Sievert). Fused pimaric acid dissolves rapidly when triturated with its own weight of cold alcohol, but the solution solidifies almost immediately, from separation of crystals. When the fused acid has again become crystalline, it requires as much alcohol to dissolve it as

the crystallised acid (Laurent). Crytals are still obtained from the alcoholic solution, even after long standing (Sievert).

*Laurent's Pyromaric acid.* — Obtained by the dry distillation of pimaric acid. When the colophony-like distillate is triturated with twice its weight of alcohol, the solution produced at first quickly becomes turbid, from separation of crystals of pyromaric acid, which are purified by washing and recrystallisation. — Triangular tables, melting at 125°, volatile without decomposition. Contains 78·27 p. c. C., and 9·90 H., or the same proportions as pimaric acid, from which it differs by the fact that when its boiling dilute alcoholic solution is mixed with neutral acetate of lead, it produces no precipitate at first, and after some time only, long needles of a lead-salt containing 26·52 p. c. oxide of lead, at 100°. The acid dissolves in 8 or 10 parts of alcohol, and very easily in ether. This acid, which Laurent found also in Paris colophony, was afterwards regarded by him as identical with sylvic acid. On the other hand, Sievert, who found pimaric acid volatile without decomposition (and susceptible of distillation? Kr.), seems to consider pyromaric acid as identical with pimaric acid, and different from sylvic acid.

## Nitromaric Acid.

$$C^{40}N^2H^{26}O^{16} = C^{40}X^2H^{26}O^2,O^6.$$
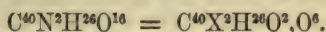
LAURENT. *Ann. Chim. Phys.* 72, 397; *Ann. Pharm.* 34, 282. — *N. Ann. Chim. Phys.* 22, 461; *J. pr. Chem.* 45, 61.

*Azomarsäure. Acide azomarique.*

*Preparation.* Pimaric acid is boiled with a large excess of nitric acid till a yellow, friable resinous mass forms on the surface of the liquid. This mass is boiled repeatedly with water, powdered, and slowly dried, at last at 100°; or it is dissolved in alcohol and precipitated by water.

Yellow, amorphous resin. Its alcoholic solution reddens litmus.

|  |  |  |  |  |  | Laurent. | | |
|  |  |  |  |  |  | *earlier.* |  | *later.* |
|---|---|---|---|---|---|---|---|---|
| 40 C | ............ | 240 | ........ | 56·87 | ........ | 56·72 | ........ | 57·0 |
| 2 N | ............ | 28 | ........ | 6·60 | ........ | 7·20 | ........ | 7·1 |
| 26 H | ............ | 26 | ........ | 6·15 | ........ | 5·60 | ........ | 5·9 |
| 16 O | ............ | 128 | ........ | 30·38 | ........ | 30·48 | ........ | 30·0 |
| $C^{40}X^2H^{26}O^8$ .... | | 422 | ........ | 100·00 | ........ | 100·00 | ........ | 100·0 |

Nitromaric acid decomposes when melted, leaving a bulky charcoal; it does not glow or explode, even when rapidly heated. — Burns like a resin. — When submitted to dry distillation, it yields a very little oil.

The acid is insoluble in *water.* — It dissolves in *oil of vitriol*, from which it is precipitated by water.

The *salts* of nitromaric acid are reddish-yellow. Those of the alkalis are soluble in water; the baryta-salt is insoluble. — A solution

of the very easily soluble ammonia-salt dries up to a reddish-yellow transparent mass.

An alcoholic solution of nitromaric acid forms yellowish precipitates with alcoholic *neutral acetate of lead* and *nitrate of silver*. The lead-salt explodes slightly when heated; it contains 32·8 to 33·4 p. c. lead, and dissolves to a slight extent in alcohol ($C^{40}X^2H^{24}Pb^3O^8 = 33.12$ p. c. Pb).

Nitromaric acid dissolves easily in *alcohol* and *ether*.

# Copaivic Acid.

$$C^{40}H^{30}O^4 = C^{40}H^{30},O^4.$$
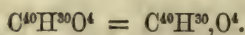
SCHWEITZER. *Pogg.* 17, 488; 21, 172.
H. ROSE. *Pogg.* 33, 35; 53, 372.
HESS. *Pogg.* 46, 324; *Ann. Pharm.* 29, 140.

*Copabavinsäure.* Occurs, together with copaiba-oil, in balsam of copaiba. See below.

Nine parts of copaiba balsam are mixed with two or more parts of aqueous ammonia of sp. gr. 0·95, and placed in the cold in closed vessels, when, after some weeks at − 10°, or in the course of a day at − 12·5°, white shining needles are formed. The solidified mixture is thrown upon a cloth; the crystals remaining are shaken with a little ether, which dissolves the copaiba balsam; and the crystals are then pressed and recrystallised from absolute alcohol, from which they separate free from ammonia (Schweitzer).

*Properties.* Transparent or translucent, colourless crystals, 4 to 6 lines long (Schweitzer). — According to G. Rose, rhombic prisms without cleavage. The angles of the obtuse lateral edges = 90° 46′; the acute lateral edges frequently truncated; two bevelling faces inclined to one another at 126° 50′ rest upon the obtuse edges. — The acid has a bitter taste, like the balsam, and a faint odour. It is heavier than water; has an acid reaction (Schweitzer; Rose).

|  |  |  |  |  |  | Rose. |  |  |  | Hess. |
|  |  |  |  |  |  | earlier. |  | later. |  |  |
| 40 C | ............. | 240 | ........ | 79·48 | ........ | 78·17 | ........ | 79·29 | ........ | 78·02 |
| 30 H | ............. | 30 | ........ | 9·93 | ........ | 10·15 | ........ | 10·31 | ........ | 10·01 |
| 4 O | ............. | 32 | ........ | 10·59 | ........ | 11·68 | ........ | 10·40 | ........ | 11·97 |
| $C^{40}H^{30}O^4$ | ........ | 302 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Isomeric with sylvic and pimaric acids.

Copaivic acid dissolves in *oil of vitriol* with red-brown colour, and carbonises when the solution is heated. — It dissolves in hot strong *nitric acid*, from which it is precipitated in white flocks by water (Schweitzer).

The acid is insoluble in *water*. — It is not precipitated from an alcoholic solution by *aqueous ammonia*; the acid thrown down from its alcoholic solution by water dissolves in ammonia. — Alcoholic *potash*

or strong aqueous potash does not precipitate the alcoholic solution of the acid, but dilute potash throws down the potash-salt.

*Lime-salt.* — Alcoholic copaivic acid is mixed with excess of chloride of calcium; ammonia is added; and the resulting precipitate is collected without access of air (Rose).

|  |  |  |  |  | Rose. |
|---|---|---|---|---|---|
| $C^{40}H^{29}O^3$ | 293 | | 91·28 | | |
| CaO | 28 | | 8·72 | | 8·32 |
| $C^{40}H^{29}CaO^4$ | 321 | | 100·00 | | |

*Lead-salt.* — The acid gives off water when heated with oxide of lead (Schweitzer). Alcoholic neutral acetate of lead throws down from an alcoholic solution of the acid, an abundant slightly crystalline precipitate. Easily fusible (Rose).

|  |  |  |  |  | Rose. |
|---|---|---|---|---|---|
| $C^{40}H^{29}O^3$ | 293 | | 72·34 | | |
| PbO | 112 | | 27·66 | | 27·53 |
| $C^{40}H^{29}PbO^4$ | 405 | | 100·60 | | |

*Silver-salt.* — Nitrate of silver in alcoholic solution mixed with alcoholic copaivic acid, forms a crystalline precipitate on addition of ammonia. — The salt turns brown in the light. It is easily fusible, and dissolves in aqueous ammonia, and with difficulty in alcohol (H. Rose).

|  |  |  |  |  | Rose. |
|---|---|---|---|---|---|
| 40 C | 240 | | 58·68 | | 57·75 |
| 29 H | 29 | | 7·09 | | 7·55 |
| 3 O | 24 | | 5·87 | | |
| AgO | 116 | | 28·36 | | 27·41 to 28·25 |
| $C^{40}H^{29}AgO^4$ | 409 | | 100·00 | | |

Copaivic acid is easily soluble in absolute *alcohol;* less freely in dilute alcohol, and in *ether.* It dissolves in volatile and fat *oils* (Schweitzer).

*Copaiba Balsam.* — From various species of *Copaïfera.* 1. *Brazilian balsam,* containing volatile oil (xiv, 286) and copaivic acid. — Pale yellow transparent oil, at first fluid, like thick oil, afterwards of the consistence of honey. Sp. gr. 0·95 (Schönberg), 0·966 (Stoltze), 0·9925 (Brandes & Reiche), 0·997 (Martins), 0·916 to 0·986 (Procter). Has a peculiar balsamic odour and a burning bitter taste. When mixed with alcohol it reddens litmus (Martins). Rotates a ray of polarised light generally to the left in varying degrees (Buignet). — When distilled with water, it yields volatile oil. With fresh balsam the remaining resin is brittle only after boiling for 20 to 24 hours, but with old balsam after 8 or 10 hours (Schweitzer). A solution of the resin in warm alcohol of 75 p. c. deposits on cooling, a brown, greasy, soft resin, which forms a milky solution with ammonia and caustic potash, dissolves in ether and alcohol (in 75 p. c. alcohol only when warmed), and in volatile and fat oils. There remains in solution a brittle, pale-yellow resin—copaivic acid. This splitting up is effected also by strong rock-oil, which dissolves the copaivic acid and leaves the soft resin undissolved (Gerber; Stoltze).

The bottom of a bottle containing copaiba balsam was found, after standing for many years, to be covered with a transparent resinous layer, together with six-sided tables and prisms (Pelletier, *J. Pharm.* 6, 315). — When heated alone to 125°, the balsam gives off only traces of oil and water; at 262° it begins to boil and yield oil, with formation of gas; and at 287° there pass over, first colourless, then yellow and dark-brown oil, whilst gases are evolved and charcoal remains (Schönberg, *A. Gehl*, 6, 493). — The balsam dissolves phosphorus easily, and, when hot, also sulphur (Gerber).

Copaiba balsam forms with a small quantity of aqueous ammonia of sp. gr. 0·95 to 0·96, a turbid mixture, but with ⅛th of ammonia a perfectly clear solution, which again becomes turbid with more than ¼th of ammonia, and gradually deposits the soap of the balsam, the supernatant liquid consisting of excess of ammonia with traces of balsam. Under these circumstances a rise of temperature of about 15° takes place. If the balsam contains fat oil, or more than ⅕th of castor-oil, it does not become clear with ¼th of ammonia at 15°. The clear mixture of balsam and ammonia may be mixed with a little water without turbidity, but with more than an equal quantity of water it becomes milky (Stoltze; Planche; Schweitzer). — The balsam is rendered turbid by dropping into it a solution containing ⅓rd of hydrate of potash, but becomes perfectly clear, with rise of temperature, when ⅓rd of its volume of the solution is added, and is again rendered turbid by a larger quantity, after which two layers are formed on standing. The soap of copaiba balsam dissolves perfectly in alcohol of 75 to 90 p. c.; when fatty oils are present, the solution deposits white flocks in a few hours (Stoltze): the soap of a balsam thus adulterated is rendered turbid by a much smaller quantity of water than that of pure balsam (Müller, *Br. Arch.* 8, 74). See also Anthon (*Repert.* 52, 331). When an alcoholic solution of the balsam is shaken with solution of caustic soda, the oil (xiv, 286) which rises to the surface removed, the soapy liquid beneath evaporated to the consistence of honey, and the soap freed from excess of alkali by means of chloride of sodium, the product, on being washed with a little water, dissolved in alcohol, and evaporated, forms a yellow, transparent soap, which dissolves in 12 parts of cold, and in 3 parts of boiling water (Ader, *J. Pharm.* 15, 95). — 100 parts of the balsam dissolve 3·1 parts of *magnesia alba* (Brandes & Gruner, *Br. Arch.* 23, 277). 8 parts of the balsam solidify to a plastic mass with 1 part of calcined magnesia (Mialbe). The compound dissolves in ether and alcohol (Gerber). The balsam hardens more rapidly with ¹⁄₁₅th of hydrate of lime than with magnesia (Thierry, *N. J. Pharm.* 1, 310). The presence of water, either in the balsam or in the lime or magnesia, is necessary for solidification; anhydrous balsam mixed with quick lime remains unchanged for a long time, but hardens in a few hours on addition of ¹⁄₃₅th of water. A homogeneous mass is produced only when water is added to the balsam or to the mixture of lime and balsam; by shaking the balsam with hydrate of lime, a granular crystalline mass is formed, on which floats the volatile oil (Roussin, *N. J. Pharm.* (4) 1, 321).

Copaiba balsam mixes with absolute alcohol; and it dissolves freely in 90 p. c. alcohol, but only to the extent of ¹⁄₁₀th or ⅑th in alcohol of 75 p. c. (Gerber). It mixes with volatile and fatty oils in all proportions, and the mixture may be added without turbidity to 2 parts of alcohol of 90 p. c., or to absolute alcohol, ether, or acetate of ethyl,

but with a larger quantity (about 8 parts) of alcohol or ether, the fatty oil is partially separated (Stoltze, *Berl. Jahrb.* 27, 2, 179). On copaiba balsam see further; Martins (*Repert.* 26, 306), Gerber (*Br. Arch.* 30, 147; 37, 36), Brandes (*Br. Arch.* 36, 351), Oberdörffer (*N. Br. Arch.* 45, 172), Stöckhardt (*N. Br. Arch.* 72, 14), Guibourt (*N. J. Pharm.* 23, 321), Procter (*Pharm. J. Trans.* 10, 603; *Pharm. Centr.* 1851, 590). — Lowe's statements (*Pharm. J. Trans.* 14, 65; *Pharm. Centr.* 1854, 653) seem to refer to Gurgun balsam.

2. *Thinner Copaiba Balsam.* — Thinner, and of a paler yellow than the former. Sp. gr. = 0·94. Remains turbid when mixed with aqueous caustic potash or ammonia, does not form a soap, and separates in a distinct layer on standing. Forms a milky solution with alcohol. — Contains 82 p. c. of paracopaiba oil, and 18 p. c. of neutral resin (Posselt).

If the residue which remains on distilling the balsam with water be boiled with water till all the volatile oils are driven off, there remains a light-brown, friable resin, a portion of which is taken up by alcohol, while another portion, nearly insoluble even in hot absolute alcohol, remains behind. — a. *The soluble resin* is pale-yellow, friable, and softens when warmed; at a higher temperature it assumes a darker colour, becomes tough, and decomposes. Neutral. Insoluble in ammonia and caustic potash, and does not precipitate acetate of copper. It is deposited from a solution in weak boiling alcohol, on cooling, in white flocks, and from strong alcohol, on evaporation only, in drops. Dissolves in ether and rock-oil. Contains, on the average, 60·62 p. c. C., 8·37 H., and 31·61 O. — b. *The insoluble resin*, purified by boiling with alcohol (whereby its bulk is diminished) and by dissolving in ether, is pale-yellow, difficultly fusible, insoluble in ammonia or caustic potash, and in weak alcohol. It is deposited in great part from a solution in a large quantity of boiling absolute alcohol on cooling, but dissolves easily in ether and rock-oil. Contains, on the average, 81·94 p. c. C., 10·52 H., and 7·54 O. (Posselt, *Ann. Pharm.* 69, 71).

*Resin of the Copaiba-balsam of Para.* Deposited, on standing, from a balsam imported in 1839, as a white, crystalline sediment, which was purified by pressing between blotting-paper, dissolving in alcohol, and allowing the solution to evaporate spontaneously. — Rhombic prisms, truncated at the acute angles, triturable to a highly electric powder. Melts at about 120°. An alcoholic solution reddens litmus.

The crystals contain, on an average, 74·83 p. c. C., 8·83 H., and 16·34 O., corresponding to the formula $C^{40}H^{28}O^6$ (75·95 p. c. C., 8·86 H.); but when a solution of the impure resin (not of the pure) in ether-alcohol is rapidly evaporated, with constant stirring, a white amorphous powder is obtained, which is nearly opaque, softens in boiling water, and contains, on the average, 71·15 p. c. C., 9·04 H., and 19·81 O., and is, therefore, a hydrate of the resin, $C^{40}H^{28}O^6,2HO$ (calc. 71·85 p. c. C., 9·00 H.).

The resin is decomposed by cold strong nitric acid, and by the dilute acid when warm, with formation of carbonic acid, nitric oxide, and two solid products, one of which is an acid free from nitrogen, soluble in water and alcohol, and forming a lead-salt which contains approximately $C^{30}H^{18}O^{14},4PbO$, while the other is a nitrogenous, very bitter, amorphous substance, the lead-salt of which contains about $C^{30}H^{18}O^{13},3PbO$. — On evaporating the resin with nitric acid, a black pitch containing humic acid is produced.

The resin forms, with soda and potash, soaps soluble in water. It remains behind unchanged on evaporating its solution in ammonia-water. — Alcoholic neutral acetate of lead throws down from an alcoholic solution of the resin mixed with a little ammonia, a white precipitate, which when washed with a little alcohol, strongly pressed, and again washed with a little alcohol, exhibits the following mean composition; but if it be washed with a large quantity of water or alcohol, the percentage of lead is altered. — The silver-salt is obtained in like manner.

|  | *Lead-salt.* |  |  |  | Fehling. |
|---|---|---|---|---|---|
| 40 C | 240 | ........ | 57·28 | ........ | 56·23 |
| 27 H | 27 | ........ | 6·44 | ........ | 6·43 |
| 5 O | 40 | ........ | 9·55 | ........ | 11·03 |
| PbO | 112 | ........ | 26·73 | ........ | 26·31 |
| $C^{40}H^{27}PbO^6$ | 419 | ........ | 100·00 | ........ | 100·00 |

|  | *Silver-salt.* |  |  |  | Fehling. |
|---|---|---|---|---|---|
| 40 C | 240 | ........ | 56·74 | ........ | 56·27 |
| 27 H | 27 | ........ | 6·39 | ........ | 6·43 |
| 5 O | 40 | ........ | 9·46 | ........ | 10·47 |
| AgO | 116 | ........ | 27·41 | ........ | 26·83 |
| $C^{40}H^{27}AgO^6$ | 423 | ........ | 100·00 | ........ | 100·00 |

The resin dissolves in alcohol and more freely in ether (Fehling, *Ann. Pharm.* 40, 110).

### Oxygen-nucleus  $C^{40}H^{22}O^8$.

## Mangostin.

$$C^{40}H^{22}O^{10} = C^{40}H^{22}O^8,O^2.$$
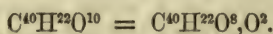
W. SCHMID.   *Ann. Pharm.* 93, 83; abstr. *Pharm. Centr.* 1855, 182; *J. pr. Chem.* 64, 254; *Chem. Soc. Q. J.*, 8, 190; *Kopp's Jahresber.* 1855, 726.

Occurs in the husks of the fruit of *Garcinia Mangostana* (Handbuch, viii, [2], 35).

*Preparation.* The husks are exhausted with hot water and boiled with alcohol; the tincture is evaporated till an amorphous, yellow mass of resin and mangostin is deposited; and this mass is dissolved in alcohol, heated to boiling, and mixed with small quantities of water till it becomes turbid. On cooling, the resin is deposited at the bottom of the vessel; and on decanting the liquid and allowing it to stand, it deposits mangostin, which, for complete purification, must be dissolved in alcohol and precipitated with basic acetate of lead. The precipitate is washed and decomposed under alcohol with hydrosulphuric acid; the filtrate, mixed with water, is set aside to crystallise; and the product is finally recrystallised from dilute alcohol.

*Properties.* Fine golden-yellow, thin laminæ, melting at 190°, without loss, to a thick yellow liquid which solidifies to a brittle, amorphous mass. When heated above its melting-point, it sublimes partly unaltered. Heavier than water; inodorous and tasteless; neutral.

|  | at 100°. |  |  | Schmid. mean. |
|---|---|---|---|---|
| 40 C ............... | 240 | ........ | 70·17 | ........ 69·67 |
| 22 H ............... | 22 | ........ | 6·43 | ........ 6·49 |
| 10 O ............... | 80 | ........ | 23·40 | ........ 23·84 |
| C⁴⁰H²²O¹⁰ ........ | 342 | ........ | 100·00 | ........ 100·00 |

$C^{40}H^{22}O^{10}$

*Decompositions.* Mangostin *burns* on platinum-foil, without leaving a residue. — It dissolves in cold *oil of vitriol* with yellowish-red colour, and carbonises in the hot liquid. — Warm *nitric acid* converts it into oxalic acid. — It reduces the oxides of the noble *metals*.

Mangostin is insoluble in *water*, but soluble with yellowish-brown colour in *alkalis*. It produces with aqueous *sesquichloride of iron*, a dark green-black coloration, which disappears on the addition of acids. It is precipitated by *basic acetate of lead*, but not by any other metallic salts.

*Mangostin with Lead-oxide.* — An excess of alcoholic mangostin, mixed with alcoholic neutral acetate of lead and a little ammonia, yields as yellow, gelatinous precipitate, triturable to a light yellowish-green powder after drying at 100°. Insoluble in water, but slightly soluble in alcohol, and (with decomposition) in acids.

|  | *Calculation according to Schmid.* |  |  | Schmid. |
|---|---|---|---|---|
| 80 C ...................... .................. | 480 | ........ | 38·37 | ........ 38·67 |
| 45 H ........................................ | 45 | ......... | 3·59 | ........ 3·45 |
| 21 O ............................... ....... | 168 | ........ | 13·46 | ........ 13·74 |
| 5 PbO ............................ ............... | 560 | ........ | 44·58 | ........ 44·14 |
| 2C⁴⁰H²²O¹⁰,5PbO + HO ............ | 1253 | ........ | 100·00 | ........ 100·00 |

$2C^{40}H^{22}O^{10}, 5PbO + HO$

Another time, when prepared in apparently the same manner, it contained 37·65 p. c. of oxide of lead.

Mangostin dissolves easily in *alcohol* and *ether*.

*Resin of Garcinia Mangostana.* — Exudes in small quantity from the tree. Fine lemon-yellow tears, of the size of peas, inodorous and tasteless. Easily pulverisable. Does not form sugar when digested with sulphuric acid. When treated with 90 p. c. alcohol, it gives up 88 p. c., which remains on evaporation as a clear amorphous mass, easily soluble in alcohol and ether, fusible at 110°, but not in boiling water. This purified resin contains 67·92 p. c. C., 6·81 H., and 25·27 O., corresponding to the formula $C^{36}H^{22}O^{20}$. It is decomposed by aqueous ammonia into alpha- and beta-resin.

α. The deep-yellow ammoniacal solution throws down, on addition of hydrochloric acid, yellow flocks of the alpha-resin which melt at 80°, and, like the purified resin, contain 67·71 p. c. C., 6·84 H., and 25·45 O. When the ammoniacal solution is precipitated by neutral acetate of lead, the yellow gummy precipitate (which is decomposible by acetic acid) contains 63·42 p. c. PbO., 24·68 C., 2·50 H., and 9·40 O., corresponding to the formula $C^{36}H^{22}O^{10}, 5PbO$.

β. The beta-resin, insoluble in ammonia, is a pale-yellow, loose

powder, melting at 115°, only partially soluble in caustic potash, but easily soluble in alcohol and ether. After drying at 100° it contains, on the average, 52·92 p. c. C., 7·88 H., and 39·20 O., corresponding to the formula $C^{36}H^{22}O^{10} + 10HO$ (Reitler, *Pharm. Viertelj.* 7, 170).

## Primary Nucleus C⁴⁰H³².

# Dammaryl.

### C⁴⁰H³².

BRANDES. *Br. Arch.* 30, 1.
BILTZ. *N. Tr.* 20, 1, 37.
DULK. *J. pr. Chem.* 45, 36.

Probably identical with Brandes' *dammarin* and Biltz's *difficultly soluble hard resin.* — Recognised as a non-oxygenised compound and investigated by Dulk. — Occurs in East Indian and probably also in Australian dammar-resin. (See below.)

Powdered dammar-resin is exhausted with warm alcohol of 82 p. c., which takes up soluble resins; the insoluble portion is treated with ether; the ethereal solution is concentrated; and the residue thrown into boiling water for a few seconds, after which the product is collected and dried, as quickly as possible in a vacuum (Dulk).

*Properties.* White, highly lustrous, amorphous powder, resembling magnesia; not electric when rubbed. Softens at 145°, and melts at 190° to a clear yellow oil (Dulk).

|  |  | at 100°. |  |  |  | Dulk. mean (7). |
|---|---|---|---|---|---|---|
| 40 C | ............... | 240 | ........ | 88·23 | ........ | 88·28 |
| 32 H | ............... | 32 | ........ | 11·77 | ........ | 11·97 |
| C⁴⁰H³² | ............ | 272 | ........ | 100·00 | ........ | 100·25 |

Dulk's formula, $C^{45}H^{36}$, is also a multiple of $C^5H^4$. Isomeric with gutta-percha and caoutchouc.

*Decompositions.* 1. Dammaryl when submitted to *dry distillation* yields an empyreumatic oil (and acetic acid) (Biltz). — 2. When heated it melts, *burns* for a long time with flame, turns brown, and burns away without leaving a residue (Brandes). — 3. It is not perceptibly acted on by cold *nitric acid,* but is converted into a yellow acid resin by the hot acid (Brandes). Strong nitric acid dissolves it, forming a reddish solution, from which water precipitates a resin, soluble, with brown-red colour, in ammonia and potash (Biltz). — 4. It is not altered by cold *oil of vitriol* at first, but afterwards turns yellow, and, when warmed, brown-red, and dissolves partially, so that water throws down white flocks from the liquid (Brandes; Biltz). — 5. When boiled with *chlorate of potash* and *hydrochloric acid,* it takes up chlorine; after 8 hours it contains 27 p. c., after 16 hours, at 110°, 33·38 p. c., and after longer treatment very little more (33·73 p. c.) chlorine ($C^{40}H^{29}Cl^3$ = 28·3 ; $C^{40}H^{28}Cl^4$ = 34·6 p. c. chlorine). The latter product gives off

water at 120°, and when further heated, hydrochloric acid [chlorous acid (Dulk)], and at 130° loses 6 to 7 p. c. of its chlorine: it turns yellow at 160°, and burns at 185° (Dulk).

*Combinations.* — *With Water?* — Dammaryl is found to contain oxygen even after short contact with air, and still more after exposure to aqueous vapour at 110°, or to warm moist air, and retains oxygen even after drying at 100° (Dulk). Dulk regards this change as an oxidation, or, as a conversion into dammarylic acid and hydrate of dammaryl: he did not, however, investigate the behaviour of the products with solvents (Kr).

|  | With 1 at. water. |  |  |  | *a.* |  | Dulk. *b.* |  | *c.* |
|---|---|---|---|---|---|---|---|---|---|
| 40 C ................ ...... | 240 | ........ | 85·41 | ........ | 85·51 | ........ | 83·29 | ........ | 82·4 |
| 33 H.................... | 33 | ........ | 11·74 | ........ | 11·77 | ........ | 11·11 | ........ | 11·5 |
| O ................... | 8 | ........ | 2·85 | ........ | 2·72 | ........ | 5·60 | ........ | 6·1 |
| $C^{40}H^{32},HO$ ........ | 281 | ......... | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·0 |

With 2 at. water.

| 40 C................................ | 240 | ............ | 82·75 |
|---|---|---|---|
| 34 H ............................ | 34 | ............ | 11·72 |
| 2 O................................ | 16 | ............ | 5·53 |
| $C^{40}H^{32},2HO$.................... | 290 | ............ | 100·00 |

Dammaryl is not perceptibly soluble in hot aqueous *phosphoric acid,* or in *acetic acid, ammonia-water,* or boiling solution of *caustic potash.*

Dammaryl is insoluble in boiling *alcohol* (Dulk): according to Brandes, it dissolves in 500 parts of boiling absolute alcohol. — It dissolves easily in cold *ether* (Dulk), in *volatile oils,* in *fat oils* when warm, and in warm *copaiba balsam* (Brandes; Biltz).

*Appendix to Dammaryl.*

## 1. Semihydrate of Dammaryl.

$$C^{80}H^{65}O = 2C^{40}H^{32},HO.$$
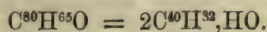
BILTZ. *N. Tr.* 20, 1, 52.
DULK, *J. pr. Chem.* 45, 41.

When dammar-resin is exhausted with alcohol and ether, this body remains behind as a grey pasty mass which persistently retains the ether, and, after drying, is shining, brittle, and easily pulverisable. It softens at 205°, and melts to a clear brown liquid at 215°. — Insoluble in alcohol, ether, acetic acid, ammonia, and potash. It dissolves slowly in hot oil of vitriol, from which it is precipitated by water as a white resin, and is completely soluble in hot oil of turpentine, more quickly in rock-oil, and slightly in oil of almonds and olive-oil (Biltz; Dulk).

|  |  | at 180°. |  |  |  | Dulk. mean (2). |
|---|---|---|---|---|---|---|
| 80 C | ................ | 480 | ........ | 86·82 | ........ | 86·52 |
| 65 H | ................ | 65 | ........ | 11·75 | ........ | 11·75 |
| O | ................ | 8 | ........ | 1·43 | ........ | 1·73 |
| $2C^{40}H^{32}$,HO | ........ | 553 | ........ | 100·00 | ........ | 100·00 |

According to Dulk, $C^{90}H^{73}O$.

2. *Dammar-resins soluble in alcohol.* — When powdered dammar-resin is treated with weak and with absolute alcohol in succession, two different resins are dissolved (Dulk's *hydrate of dammarylic acid* and *anhydrous dammarylic acid*), whilst dammaryl and semihydrate of dammaryl remain undissolved. — *a.* The resin extracted by weak alcohol, when freed from adhering alcohol by boiling with water and dried, is a white, soft, very electric powder, melting at 56° to a deep-yellow oil, which floats on water, and does not absorb oxygen from the air at 45°. In alcoholic solution it reddens litmus slightly. — *b.* The resin extracted by absolute alcohol resembles *a*, but is whiter, melts at 60°, and reddens litmus strongly. — *c.* Hot alcohol of 65 p. c., used for extracting dammar, deposits *c* in the form of a white powder on cooling (Dulk).

*Analyses by Dulk, at a mean temperature of 50°.*

|  |  | *a.* |  | *b.* |  | *c.* |
|---|---|---|---|---|---|---|
| C | ................ | 79·45 | ........ | 81·81 | ........ | 80·19 |
| H | ................ | 10·75 | ........ | 11·10 | ........ | 10·95 |
| O | ................ | 9·80 | ........ | 7·09 | ........ | 8·86 |
|  |  | 100·00 | ........ | 100·00 | ........ | 100·00 |

*a* is hydrate of dammarylic acid, $C^{45}H^{37}O^4$, *b* dammarylic acid $C^{45}H^{36}O^3$, and *c* a mixture of the two (Dulk).

*a* and *b* form with bases corresponding salts, which, however, are not obtained in the crystalline state, and contain very varying proportions of base. The potash-salt is brown, soluble in alcohol and ether, and contains 2·03 and also 4·38 and 6·15 p. c. KO. — *a* does not precipitate either neutral or ammoniacal nitrate of silver; but nitrate of silver produces in a strong warm alcoholic solution of *b*, a whitish-yellow precipitate containing, at 100°, 16·38 p. c. AgO: the alcoholic washings deposit a pure yellow silver-salt containing 14·64 p. c. AgO. Other silver-salts contained only 10·73 and 7·86 p. c. AgO (Dulk).

## 3. Dammar-resin.

LUCANUS. *Schw.* 56, 60.
BRANDES. *Br. Arch.* 30, 1.
BILTZ. *N. Tr.* 20, 1, 37.
GIESEKE. *N. Br. Arch.* 18, 189.
THOMPSON. *N. Ann. Chim. Phys.* 9, 499; *Phil. Mag.* 23, 81; *Ann. Pharm.* 47, 351.
SCHRÖTTER. *Pogg.* 59, 72.
A. DULK. *J. pr. Chem.* 45, 16.

The dammar-resin occurring in commerce is of various sorts,

the East Indian and Australian being the most abundant. See Guibourt (*Rev. Scient.* 16, 177). — The *East Indian*, or *Dammar-puti*, from *Pinus Dammara*, Lamb., occurs in pieces varying from the size of a pea to that of the fist: it is whitish-yellow, clear and translucent, sometimes covered with a white dust. It is easily broken, and exhibits a shining conchoïdal fracture. Nearly inodorous and tasteless, and does not soften between the teeth. Sp. gr. 1·04 to 1·05 (Biltz), 1·06 (Lucanus), 1·097 to 1·123 (Brandes). Melts at 73° (Dulk): becomes viscid at 100°, and melts at a higher temperature, more easily than mastic, less easily than colophony (Biltz). Softens at 75°, forms a thick liquid at 100°, and is clear and limpid at 150° (Schrötter.) — Its alcoholic solution reddens litmus (Lucanus). — *Australian* or *New Zealand dammar-resin*, from *Dammara Australis*, occurs in masses of the size of the fist or larger, composed of an internal milk-white portion covered with a transparent layer, which is again covered with an opaque outer layer. It is of a pale amber-yellow colour, exhibits a conchoïdal fracture, and softens somewhat between the teeth. Melts under hot water to a viscid mass. Emits an odour of turpentine when rubbed (Guibourt).

*Analyses of the entire resin.*

|   | Schrötter. mean, at 100°. | | Thompson. *a.* | | *b.* | | Dulk. mean, at 50°. |
|---|---|---|---|---|---|---|---|
| C | 81·96 | ........ | 74·45 | ........ | 75·46 | ........ | 82·53 |
| H | 11·18 | ........ | 10·28 | ........ | 9·76 | ........ | 11·29 |
| O | 6·86 | ........ | 15·27 | ........ | 14·78 | ........ | 6·18 |
|   | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Thompson's analyses appear to differ from the others, not so much from his having investigated Australian, and the others East Indian dammar, as because his analyses were made with oxide of copper, without oxygen. Moreover, the resin *b*, melted at 176°, was doubtless decomposed.

Dammar-resin, subjected to *dry distillation*, yields [no umbelliferous (Sommer), and no hydrosulphuric acid (Bandrimont)] acetic acid, volatile oil, and a yellowish resinous sublimate, leaving a residue of charcoal (Lucanus). Thompson obtained, by dry distillation, an empyreumatic oil (his *dammaröl*) containing 82·22 p. c. C., 11·14 H., and 6·64 O., corresponding to the formula, $C^{40}H^{28}O^3$; by dry distillation with 6 parts of lime, a thick oil boiling at 132°, called *dammarone* is obtained ; it contains 86·22 p. c. C., 11·53 H., and 2·25 O., corresponding to the formula, $C^{38}H^{30}O$. — *Water* takes up from dammar small quantities of vegetable acids and sulphate of lime (Biltz). — *Oil of vitriol* dissolves it completely, forming a yellow, or purple-red, or with more dammar, a black solution, from which water throws down a whitish-yellow mass, somewhat less easily fusible than dammar, but behaving in the same way with ether and alcohol (Dulk). — Dammar-resin is dissolved and decomposed by *nitric acid*. — The resin, suspended in boiling water and treated for several hours with *chlorine*, is converted into a whitish-yellow frothy mass containing 26 p. c. chlorine, and does not undergo further change. — When heated with soda-lime, at last to 320°, dammar evolves hydrogen and hydrocarbons : the resin separated from the residue by hydrochloric acid is more difficultly fusible than before ; insoluble in potash and ammonia, but almost entirely soluble in absolute alcohol. An odour of valerianic acid is evolved in the

process (Dulk). — Dammar-resin is not attacked by warm acetic acid, hydrochloric acid, ammonia-water, or caustic potash, though, according to Lucanus, it increases in weight in the last-named liquid, and after the solution has been poured off, is found to be partially soluble in water.

Besides 0·2 p. c. of mineral substances, and 0·1 p. c. of gum, dammar contains the following bodies: $a$, a hydrocarbon, viz., dammaryl (p. 332); $b$ and $c$, resins soluble in alcohol, hydrated and anhydrous dammarylic acid; and $d$, semi-hydrate of dammaryl (p. 333). Of these constituents, $d$ (amounting to 6 or 8 per cent.), is insoluble in ether and absolute alcohol; $b$ is dissolved by the first treatment with weak alcohol, together with portions of $c$, which is completely extracted by absolute alcohol, whilst a mixture of $a$ and $d$, separable by ether, remains behind. As, however, dammaryl takes up oxygen and water from the air (becoming insoluble?) different quantities of it are obtained according to the method of treatment adopted (Dulk). — $\alpha$. Cold ether dissolves 98 p. c. of the powdered resin, leaving $d$. — $\beta$. Boiling absolute alcohol takes up 80 to 84 p. c. — $\gamma$. The powdered resin, treated with weak alcohol, gives up to that liquid 36 p. c. of dammarylic acid; absolute alcohol then takes up 43 p. c. of anhydrous dammarylic acid, leaving a mixture of 13 p. c. of dammaryl soluble in ether, and 8 p. c. of semi-hydrate of dammaryl insoluble in ether. — $\delta$. Alcohol of 65 or 82 degrees dissolves the hydrated together with a portion of the anhydrous acid; when employed boiling, it deposits a mixture of the two on cooling (Dulk).

Lucanus found dammar soluble to the extent of one-half in absolute alcohol, whilst with alcohol of 80 p. c., $\frac{1}{3}$th was soluble in the cold, and $\frac{1}{4}$th in the hot liquid. — Brandes obtained from dammar 83·1 p. c., easily soluble in alcohol, and 16·8 p. c. of a difficultly soluble resin. Biltz obtained 72·5 p. c., easily soluble in 80 p. c. alcohol, 22·5 p. c., difficultly soluble in hot absolute alcohol and ether, and 5 p. c. of insoluble resin. Thompson separated Australian dammar-resin, by boiling it with weak alcohol, into *dammaran*, which remained behind, and *dammaric acid*, which dissolved and was precipitated from the solution by water. The latter body separates from alcohol in crystalline granules, reddens litmus, and contains, at 100°, 76·29 p. c. C., 9·31 H., and 18·00 O., corresponding to the formula, $C^{40}H^{31}O^{7}$. It dissolves in ammonia, and forms a silver-salt (which may be precipitated from the ammoniacal solution by nitrate of silver) containing 64·78 p. c. C., 9·01 H., 11·61 O., and 14·60 AgO. — Dammaran is a white brittle resin, containing, at 100°, 75·02 p. c. C., 9·60 H., 15·38 O., corresponding to the formula, $C^{40}H^{31}O^{6}$; it absorbs oxygen when heated to 150°—175°. Forms colourless solutions with absolute alcohol and oil of turpentine (Thompson). These analyses and statements do not appear to be very trustworthy (Kr.).

Dammar dissolves very slightly in *acetone* (Wiederhold), completely in *volatile* and *fat oils* (Dulk), but, according to Stickel, not perceptibly in *castor-oil*. According to Guibourt, *oil of turpentine* does not dissolve East Indian dammar completely (contrary to Brandes and Lucanus), and leaves 80 p. c. of Australian dammar undissolved.

# Gutta (Gutta-percha).

## $C^{40}H^{32}$.

SOUBÉIRAN. *N. J. Pharm.* 11, 17; *J. pr. Chem.* 39, 373; *Dingl. Polyt. J.* 103, 415; *Ann. Pharm.* 64, 380; *Kopp's Jahresber.* 1847 and 1848, 743.

KENT. *Sill. Am. J.* (3), 6, 246; *Kopp's Jahresber.* 1847 and 1848, 744.

ADRIANI. *Kopp's Jahresber.* 1850, 519; *Pharm. Centr.* 1851, 17; abstr. from *Verhandl. over de Gutta Percha en Caoutschouc.* Utrecht, 1850. — *Chem. News*, 2, 277, 289, and 318; *Kopp's Jahresber.* 1860, 496.

D. MACLAGAN. *N. Ed. Phil. J.*, 39, 238.

ARPPE. *J. pr. Chem.* 53, 171; *Kopp's Jahresber.* 1851, 530.

PAYEN. *Compt. rend.* 35, 109; *J. pr. Chem.* 57, 152; *Kopp's Jahresber.* 1852, 637. — *Rép. Chim. appliquée.* 1, 517; *Kopp's Jahresber.* 1859, 519.

BAUMHAUER. *J. pr. Chem.* 78, 277; *Chem. Centr.* 1860, 186; *Kopp's Jahresber.* 1859, 518.

A. W. HOFMANN. *Ann. Pharm.* 115, 297; *Kopp's Jahresber.* 1859, 517.

OUDEMANNS. *Scheik. Onderz.* 2 Deel, 3 Stuk, *Onderz.* 291; *Kopp's Jahresber.* 1859, 517.

W. A. MILLER. *Chem. Soc. Qu. J.* [2], 3, 273.

The hydrocarbon $C^{40}H^{32}$ (or $C^{40}H^{30}$, according to Miller), the pure gutta, forms the principal constituent of the hardened sap of *Isonandra Gutta*, which occurs in commerce as gutta-percha.

*Separation from Gutta-percha.* Gutta-percha, purified by treating it with water and hydrochloric acid, is dissolved in boiling ether; the mass which separates on cooling is quickly pressed, and dissolved in boiling ether; and the portion again deposited is washed with cold ether and alcohol: it then becomes gelatinous. The expressed mass is at once melted by heating to 100°, to prevent oxidation, and dried (Baumhauer).

The following methods also seem to yield pure gutta, although the products investigated were already changed by oxidation.

1. Comminuted gutta-percha is treated with cold ether, or with boiling absolute alcohol, so long as these liquids take up anything: the residue is pure gutta: the filtrate deposits *alban*, whilst *fluavil* remains in solution (Payen). — 2. Gutta-percha is treated in succession with boiling water, which takes up acids and a brown extract, with boiling alcohol, which extracts a soft resin, and with ether, which dissolves a yellowish-white resin; the residue is dissolved in oil of turpentine, and precipitated with alcohol, and the precipitate is washed with boiling alcohol (Soubeiran. Adriani and Geiseler adopt a similar process. — 3. Gutta-percha, previously treated with water, alcohol and ether, is dissolved in chloroform and precipitated by alcohol (Adriani). As the solution cannot be filtered when it contains more than 1 part of gutta-percha in 40 parts of chloroform, and as the strong solution clarifies very slowly by standing, Maschke (*N. Br. Arch.* 89, 31) shakes the solution with

a little water, which takes up the impurities, and, after allowing it to stand for 14 days, draws off the clear lower layer. The solution may be decolorised with animal charcoal; alcohol and ether also extract the brown colour from gutta-percha which has been dissolved in alcohol and recovered from the solution by distillation, taking up at the same time alban and fluavil (Maschke).

*Properties.* White, fine powder, becoming transparent at 100°, melting to a viscid mass at 150° and decomposing at higher temperatures (Baumhauer). The residue which remains on exhausting gutta-percha with boiling alcohol, or with ether, is white and opaque, or semi-translucent in the cold, and translucent at 100°, at which temperature it runs together; at 10° to 30° it is soft, tough, ductile, and slightly elastic. After the removal of air-bubbles, it is heavier than water (Payen).

| | | | Baum-hauer. | Hofmann. | Adriani. | Mac-lagan. | Soubeiran. |
|---|---|---|---|---|---|---|---|
| 40 C | 240 | | 88·23 | 88·02 | 88·12 | 87·91 | 86·36 | 83·47 |
| 32 H | 32 | | 11·77 | 11·88 | 12·49 | 11·94 | 12·15 | 11·47 |
| C⁴⁰H³² | 272 | | 100·00 | 99·90 | 100·61 | 99·85 | 98·51 | 94·94 |

| | | | | Miller. |
|---|---|---|---|---|
| Or : 40 C | 240 | | 88·88 | 88·96 |
| 30 H | 30 | | 11·12 | 11·04 |
| C⁴⁰H³⁰ | 270 | | 100·00 | 100·00 |

Isomeric with dammaryl (p. 332) and caoutchouc (p. 343).

*Decompositions.* 1. Gutta very readily absorbs oxygen, especially when in powder, whether in the pure state or as a constituent of commercial gutta-percha, formic acid being thereby produced (Baumhauer). — *a.* Gutta prepared as above and dried in powder, whereby it becomes transparent, exhibits the composition *a.* — *b.* Gutta prepared in a similar manner was almost entirely soluble in cold ether after drying (*b*). — *c.* When gutta-percha, purified by kneading with water, washing with hydrochloric acid, and drying in the air or over oil of vitriol, is powdered, exhausted with cold alcohol, and dissolved in chloroform, alcohol throws down from the solution a fine powder, which, when exhausted with cold alcohol and dried in a vacuum, exhibits the composition *c.* When again exhausted with alcohol it gives up to that liquid a pale-brown resin, which may be obtained by recrystallisation in the form of a white, somewhat crystalline mass (*e*): *d* remains undissolved (Baumhauer).

| | *a.* | *b.* | *c.* | *d.* | *e.* |
|---|---|---|---|---|---|
| C | 86·80 | 83·49 | 68·81 | 67·71 | 83·19 |
| H | 11·72 | 11·25 | 9·46 | 9·41 | 10·34 |
| O | 1·48 | 5·26 | 21·73 | 23·12 | 6·47 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

Baumhauer gives for *b* the formula C²⁰H¹⁶O.

To such an oxidation is owing the brittleness of manufactured

gutta-percha, which thereby loses its cohesion and exhibits an altered behaviour with ether and alcohol. *a*. Cold alcohol takes up from the altered gutta-percha a brown resin, triturable to a powder after drying over oil of vitriol and at 100° (at which temperature it melts), and containing, on an average, 62·79 p. c. C., 9·29 H., and 27·92 O. — *b*. From the residue freed from *a*, boiling alcohol takes up a similar resin, containing 67·72 p. c. C., 10·09 H., and 22·19 O. — *c*. The residue exhibits the composition of pure gutta (given above), and dissolves in ether, chloroform, and benzene (A. W. Hofmann).

When thin sheets of white, flexible, gutta-percha, perfectly soluble in bisulphide of carbon, are frequently moistened and dried, and exposed to temperatures varying between 10° and 50°, the gutta-percha hardens to a yellow brittle substance, which dissolves partially in alcohol and ether, and has become partially insoluble in bisulphide of carbon. The portion taken up by alcohol resembles fluavil; that soluble in ether is granular, yellow, and scarcely fusible at 100°; the portion dissolved by bisulphide of carbon is soft, white, and ductile, like gutta-percha. The portion remaining undissolved is yellow and brittle; it swells in chloroform, benzene, and oil of turpentine, and shrinks in ammonia-water and acetic acid (Payen).

¶ From Miller's experiments it appears that gutta-percha may be preserved for months and even years with little change, either in air or water, provided light be excluded; sea-water appears to be particularly well adapted for its preservation. But alternate exposure to moisture and dryness, especially if the sun's light has also access to it, rapidly destroys gutta-percha, rendering it brittle, friable, and resinous. A gradual absorption of oxygen takes place, and the gutta-percha slowly increases in weight, becoming at the same time proportionately soluble in alcohol and in dilute solutions of the alkalis. Some portion of the gutta, however, always remains unchanged. ¶

Pure gutta is violently acted on by *ozone*. — It decomposes at a temperature of 180°, evolves bubbles of vapour at 210°, and begins to froth up at 280° (Baumhauer). By dry distillation gaseous and liquid hydrocarbons are produced (Payen). — *Nitric acid* forms hydrocyanic and formic acids (Oudemanns). — In *hydrochloric acid gas* gutta assumes a brown-black colour, melts superficially, and takes up hydrochloric acid. When dry hydrochloric acid gas is passed over gutta-percha previously purified with water and hydrochloric acid, and the brown mass thereby formed is boiled with ether, which dissolves the greater part, the brown portion remaining undissolved contains, at 100°, 72·98 p. c. C., 9·05 H., 3·86 Cl., and 14·11 O. On evaporating the ethereal solution, exhausting the residue with cold alcohol, evaporating, again dissolving in boiling alcohol, and cooling the solution, a brown, elastic, sticky mass is thrown down, containing 83·54 p. c. C., 11·49 H., and 5·26 Cl., corresponding to the formula $C^{100}H^{80}.HCl$ (Baumhauer). — Gutta turns brown in *oil of vitriol*, evolving sulphurous acid (Payen).

Gutta is insoluble in *alcohol* and cold *ether* (see above), but easily soluble in *bisulphide of carbon* and *chloroform*. It dissolves very slightly in *benzene* at 0°, but more freely at 25°: the solution saturated at 30° solidifies to a semi-transparent mass on cooling. It is scarcely soluble in *oil of turpentine* at 0°, but becomes suspended in the liquid, and dissolves on warming (Payen). See also Gutta-percha.

## Gutta-percha of Commerce.

The hardened sap of *Isonandra Gutta*, an East Indian tree of the sapotaceous order. *Sapota Muelleri* also yields gutta-percha (Bleek-rode). The sap, which is fluid at first, solidifies to a yellow spongy mass on boiling (Oxley, *N. Ed. Phil. J.* 44, 286), or even when kept in bottles (Baumhauer). A sap of this kind, altered a little by transport, but otherwise in a natural state, yielded, on addition of $\frac{6}{10}$ths of alcohol, 14·3 p. c. of pure white gutta-percha, the colouring matter remaining dissolved in the alcohol (Bleekrode). — The sap is dried in thin layers; or the imported gutta-percha is purified by rasping it in cold water, whereby the organic matters and salts are removed, and the separation of pieces of wood and earthy impurities is facilitated. It is finally washed in warm water, dried in vessels heated to 110°, and kneaded together (Payen).

*Getah Malabeoya* is a sap resembling gutta-percha, obtained from Palembang. It melts at 170°, and forms, with boiling water, a neutral milky liquid, precipitable by alcohol. It is soluble in chloroform (Adriani, *Kopp's Jahresber.* 1850, 522). Concerning the *Getah Lahoe* of India, see under Wax.

Gutta-percha is pale-yellow or grey-white, or is coloured reddish-brown by pieces of bark falling into the sap. It is nearly as hard as wood, and tough and flexible between 0° and 25°. At 48° it becomes pasty, and at 45° to 60° may be drawn out into sheets, threads, and tubes, whereby it becomes fibrous, but not so elastic as caoutchouc; on cooling it again becomes hard. Softens in hot water, and may be moulded into forms which it retains in the cold. — Strongly electric when rubbed. Sp. gr. 0·9795 (Soubeiran), 0·966 to 0·999 (Adriani), 0·979, but heavier than water when completely freed from air (Payen). Nearly inodorous.

The gutta-percha of commerce is a mixture of pure gutta, casein, a vegetable acid, a resin soluble in ether and oil of turpentine, and another resin soluble in alcohol (Soubeiran). It contains 5·18 p. c. of ash (Adriani). Contains 75 to 82 p. c. of pure gutta, 16 to 14 p. c. of alban, and to 6 to 4 p. c. of fluavil, besides small quantities of salts, fat, volatile oil, colouring matter, and nitrogenous vegetable substances (Payen).

¶ Miller found in a sample of good commercial gutta-percha taken from a new cable, pure gutta 79·70 p. c., soft resin 15·10, vegetable fibre 2·18, moisture 2·50, and ash 0·52. The moisture was mechanically diffused through the mass, and seems to have some influence on its pliability and toughness. 100 pts. of the commercial sample, dried at 100° till it ceased to lose weight, contained (deducting the ash) 84·66 p. c. C., 11·15 H., and 4·19 O. This gutta-percha softens and liquefies at 100°. It is soluble, with the exception of a few flocks of fibrous matter, in benzene, bisulphide of carbon and ether. Alcohol dissolves none of the pure gutta, but extracts a portion of the soft resin. This resin is an oxidised compound, probably in a transitional state to a higher degree of oxidation. It was found to contain 76·65 p. c. C., 11·16 H., and 12·69 O. The true gutta was extracted nearly pure from the above-mentioned commercial sample by dissolving it in benzene, filtering, and adding alcohol, whereby a coagulum of

nearly pure gutta was separated, containing 87·22 p. c. C., 12·04 H., and 0·74 O., the small quantity of oxygen being probably due to a small portion of the resin precipitated at the same time. ¶

According to Arppe (*J. pr. Chem.* 53, 171; *Kopp's Jahresb.* 1851, 530, gutta-percha contains chips, sand, and similar bodies, salts of apocrenic acid, and six different resins, which may be separated as follows: Gutta-percha is purified by softening it in boiling water, digesting it repeatedly with alcohol of sp. gr. 0·81, and evaporating the solution. The residue consists of a mixture of resins, which are dissolved by ether, with the exception of alpha-resin. The ethereal solution is evaporated; the semifluid, sticky residue is boiled with alcohol; and the solution is filtered from the undissolved portion, which appears to be a compound of delta-resin with lime. The ethereal solution leaves on evaporation a mixture of sticky gamma-resin and crystalline beta-resin, separable by cold absolute alcohol, which leaves the latter undissolved. — The gutta-percha exhausted by boiling alcohol of sp. gr. 0·81 gives up to alcohol of sp. gr. 0·83 a further portion of delta-resin, while there remains undissolved a mixture of epsilon- and eta-resin, the former of which is more easily soluble than the latter in ether. — *Alpha-resin* is white, difficultly fusible, and may be obtained from alcohol in indistinct crystals. — *Beta-resin*, $C^{40}H^{62}O^6$, forms long needles, melting at 125°, and solidifying on cooling to a colourless glass, soluble in alcohol. — *Gamma-resin*, $C^{40}H^{62}O^3$, is pale-brown, sticky, and fusible at 50°; in water it is converted into white flocks, which are difficultly soluble in alcohol. Its solution is precipitated by neutral acetate of lead. — *Delta-resin*, $C^{40}H^{48}O^8$, forms colourless granules, melting at 175°, easily soluble in ether, difficultly soluble in absolute alcohol, and not precipitable by neutral acetate of lead. — *Epsilon-resin*, $C^{40}H^{48}O^{10}$, is a white powder, melting at 55°, precipitable from its ethereal solution by alcohol. — *Eta-resin*, $C^{40}H^{62}O$, is white and soft, ropy at 40°, brown at 110°, and brick-red after cooling. It is nearly insoluble in cold ether, and very slightly soluble in boiling alcohol: it forms the principal part of gutta-percha. Epsilon- and eta-resins are inflamed by strong nitric acid, and oxidised by weaker acid, with formation of picric acid. Thus, according to Arppe, whose work is before me only in extracts (Kr.).

Gutta-percha yields by *dry distillation*, first a clear yellow, then a dark oil, of variable boiling-point and sp. gr. 0·909, amounting altogether to 57·66 per cent. (Adriani). The oil contains 10 at. C. to 8 at. H. (Maclagan). The dry distillation of gutta-percha proceeds in the same way as that of caoutchouc, yielding a little acid water, volatile bases, hevene (see under Caoutchouc), and a little isoprene and caoutchin, together with an empyreumatic product, which may be removed by rectifying the distillate over caustic potash (Williams). — Gutta-percha is very inflammable, and *burns* with a bright flame (Oxley). — *Oil of vitriol* carbonises and corrodes gutta-percha, evolving sulphurous acid. — *Nitric acid* softens gutta-percha and dissolves it on boiling, whereupon water throws down a soft yellow resin; ultimately camphretic acid and the decomposition-products of albumin are formed (Schwanert, *Ann. Pharm.* 128, 124). — *Strong hydrochloric acid* attacks gutta-percha slowly at 20°, rendering it brown and brittle (Payen).

Gutta-percha is insoluble in *water*, though boiling water takes up from it an acid (Adriani) and a brown extract (Soubeiran). — It is insoluble in *acids* and *alkalis*. Liquid *carbonic acid* extracts brown

colouring matter, and leaves the undissolved portion white as before (Gore, *Chim. pure.* 3, 214). — *Bisulphide of carbon* dissolves gutta-percha even in the cold, with the exception of a brown substance (Payen), and leaves it unchanged and not viscid on evaporation. The solution can be filtered only when not more than 1 part of gutta-percha is dissolved in 12 parts of the bisulphide (Gieseler, *N. Br. Arch.* 83, 9). The pale-brown solution renders paper and wood water-proof (Vogel, *Repert.* 98, 402). — Gutta-percha does not dissolve, or dissolves only to the extent of 22 per cent. (Payen) in absolute *alcohol;* moreover, alcohol precipitates most of the other solutions. See above. — It is insoluble in *nitrous ether* (*J. Chim. méd.* 24, 436) and in *acetic acid.* *Ether* softens it in the cold, and dissolves it on warming (Soubeiran). Vogel found gutta-percha insoluble ; Kent found it slightly soluble ; Payen, soluble to the extent of 22 p. c. only, in ether ; Schwerdtfeger found it only partially soluble even in boiling ether ; Maclagan and Hofmann, on the contrary, found it soluble in ether. Gutta-percha purified by kneading with water and washing with hydrochloric acid, and dried, dissolves, with the exception of brown flocks, in boiling ether, the solution solidifying to a jelly on cooling (Baumhauer).

Gutta-percha dissolves easily in *chloroform* ; the solution cannot be filtered when it contains more than 1 part of gutta-percha in 16 parts of chloroform. The solution, mixed with 3 parts of ether and kept for some time below 15°, deposits the gutta-percha in the form of a white powder (Kent). The solution in chloroform is precipitable by alcohol, but not by ether (Schwerdtfeger). *Glycerin* containing acetic acid or tartaric acid dissolves gutta-percha when heated over the water-bath (Dullo, *Polyt. Notizbl.* 20, 91).

Gutta-percha dissolves in *benzene* (Mansfield) ; it dissolves only partially in benzene and *oil of turpentine* in the cold, but almost completely on warming (Payen). *Rock oil, coal-tar oil, resin oil,* the *empyreumatic oils of caoutchouc* and *gutta-percha, terebene,* and *hydrochlorate of terebene* dissolve gutta-percha, and leave it unchanged on evaporation, but if oil of turpentine containing resins is employed, it remains in a sticky state. *Olive oil* is without action on gutta-percha in the cold ; the hot oil dissolves a little, and deposits it again on cooling (Payen).

¶ On exposing samples of sheet gutta-percha for nine months to the action of *linseed oil,* boiled and unboiled *Stockholm tar,* and *coal-tar,* it was found that these liquids had not exerted any perceptible solvent action upon the gutta, which retained its texture and tenacity in all those portions which had been fairly submerged in the liquid, and protected from the light and atmospheric air ; but in those portions which had projected into the atmospheric air contained in the jar, where it was also exposed to the effects of diffused daylight, the texture had become rotten, and the material more or less brittle and resinous. These liquids exclude oxygen from the gutta-percha, and are thus enabled to exert a preservative influence upon it, without, however, in any degree softening or dissolving its texture. Hence they are likely to be highly valuable agents in coating the insulating material of telegraphic cables (Miller). ¶

*Alban.* Light, pulverulent mass, made up of microscopic, transparent laminæ (Payen). At ordinary temperatures its composition agrees with the formula $C^{20}H^{16}O^2$ ; at 130° it is represented by the formula $C^{20}H^{15}O$ (Oudemanns). — Melts at 140° (Oudemanns), at 160° to 180°,

to a transparent oil, which remains transparent on cooling, and solidi-
fies to a cracked mass a little heavier than water (Payen). It is not
attacked by cold or boiling water, or by caustic potash or dilute acids.
Strong sulphuric and nitric acids act violently upon it, as upon gutta-
percha; hydrochloric acid is without action. — Alban dissolves very
easily in bisulphide of carbon, chloroform, benzene, oil of turpentine,
and ether, crystallising from the latter on evaporation in long, pearly
laminæ. It dissolves freely in warm absolute alcohol, crystallising
from the solution on cooling, and also on evaporation (Payen).
According to Oudemanns, it dissolves in 196 parts of cold, and 19 parts
of boiling alcohol.

*Fluavil.* When freed from alcohol, which it obstinately retains,
by heating to 100° in a vacuum till frothing ceases, it is a lemon-
yellow, amorphous mass, solid and brittle at 0°, pasty at 50°, melting
at 100° to 110° (Payen). According to Oudemanns, it is $C^{20}H^{16}O$. —
Boils when strongly heated, undergoing decomposition. Violently
attacked by oil of vitriol and strong nitric acid, but not decomposed by
hydrochloric acid, ammonia, or alkalis. — Dissolves in cold bisulphide
of carbon, chloroform, alcohol, ether, benzene, and oil of turpentine,
and is left in an amorphous state on evaporation; under favourable
conditions, however, it appears to crystallise (Payen).

## Caoutchouc.

### $C^{40}H^{32}$.

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HIMLY.   *Dissert. de Caoutschouc ejusdem destill. sicc. productis.* Göttingen 1835, abstr. *Ann. Pharm.* 27, 40.

DALTON.   *Phil. Mag.* 9, 479 ;   *J. pr. Chem.* 10, 120.

BOUCHARDAT.   *J. Pharm.* 23, 454 ; *J. pr. Chem.* 36, 313 ; *Ann. Pharm.* 27, 30.

GR. WILLIAMS.   *Phil. Trans.* 10, 516 ;   *Phil. Mag.* [4] 21, 463 ; *J. pr.* 73, 188 ; *Rép. Chim. pure* 3, 200 ; Complete :   *Chem. Soc. Qu. J.* 15, 110 ; abstr. *Chem. Centr.* 1862, 833 ; *Kopp's Jahresber.* 1860, 494.

*Federharz.   Gummi elasticum.   India-rubber.* — First made known in Europe by Bouguer and Condamine in 1736. — The milky juices of the most various plants, according to Schleiden all milky saps, contain caoutchouc.   The inspissated sap of the following plants forms the caoutchouc of commerce, which comes from the northern part of South America, from the East Indies and the Sunda Islands, as well as from Madagascar.   A. *America.*   The Euphorbiaceæ : *Siphonia elastica, S. lutea,* and *S. brevifolia;* the Apocynaceæ : *Hancornia speciosa* ; the Arto-carpaceæ : *Artocarpus integrifolia, Castilleja elastica, Cecropia peltata,* also *Polletri Sapotea Mülleriana.* — B. *India.*   The Apocynaceæ : *Urceola elastica;* Artocarpaceæ : *Ficus elastica, F. indica,* and *F. religiosa.* — C. *Madagascar.   Vahea gummifera,* of the apocynaceous order.

The caoutchouc of opium possesses the same properties as com-mercial caoutchouc, but dissolves more easily in ether and in volatile and fixed oils, probably on account of its finer state of division.   It contains 87·89 p. c. C., and 12·11 H. (Pelletier, *Ann. Chim. Phys.* 50, 277 ; *Ann. Pharm.* 5, 177).   See also Buchholz (*N. Tr.* 8, 1, 37).

The dried saps of *Ficus Carica, Euphorbia Cyparissias* and *E. off., Papaver somniferum, Asclepias syriaca, A. gigantea, Lactuca sativa, Cichorium Intybus,* several species of *Sonchus* and other plants, yield caoutchouc-like substances, which remain on exhausting the dried sap with water and alcohol, or may be precipitated from an ethereal solution by alcohol : *Native Caoutchouc.*   See Carradori (*Ann. Chim. Phys.* 26, 58), Ricord Madiana (*J. Pharm.* 16, 107).   The substance obtained from *Ficus Carica* appears, according to Bizio (*Brugn. Giorn.* 20, 41), to be identical with viscin.

The sap of the *Ficus elastica* cultivated in Germany contained in 1827, a colourless, soft resin, gum, and viscin ; the same substances were found also in 1835 in the sap which exuded from the cut ends of young green twigs of the same tree ; but the less fluid sap flowing from incisions made in the stem of the tree dried up quickly to caout-chouc (Nesenbeck & Marquart). — The sap of *Ficus elastica* contains a larger quantity of water, the farther from the root it is extracted.   The sap of the terminal buds contained 17·7 p. c., that of the parts immediately below 20·98 p. c., and that from still lower 25·15 p. c. of solid con-stituents, 9·57, p. c. of those from the sap of the terminal buds con sisting of caoutchouc (Adriani).

The sap of *Siphonia elastica* conveyed in a nearly unaltered condition, in closed vessels, from South America to England contained 31·7 p. c. of caoutchouc, besides wax, bitter substance, gum, albumin, and 56·4 p. c. of water, with salts and acetic acid.   It formed a pale-yellow, thick, homogeneous cream, of sp. gr. 1·012, having an acid odour like that of spoilt milk.   When left at rest, it separated into a lower dark-brown transparent liquid, and an upper white, opaque, creamy portion.   In

thin layers it dried up to ordinary caoutchouc in the air. When heated it curdled instantaneously from separation of caoutchouc; the addition of a large quantity of alcohol, but not of water or aqueous alkalis, also threw down the caoutchouc (Faraday). Fresh caoutchouc-sap curdles in the air, like milk turning sour; the separation being hastened by the addition of hydrochloric acid or chloride of sodium. It may be preserved, mixed with $\frac{1}{15}$th of ammonia-water, in air-tight vessels filled with the liquid (Johnson, *Dingl.* 130, 156) Boussingault & Rivero (*Ann. Chim. Phys.* 23, 220), examined a sap from Mexico, the caoutchouc of which was completely precipitable by ammonia. — The reddish-white caoutchouc-sap kept in bottles turns brown-red in the air (Baumhauer).

On fig-tree sap, see Bizio (*Br. Arch.* 22, 158), Trémolière (*Bull. Pharm.* 6, 316), Landerer (*Repert.* 72, 353; 84, 70): on the sap of *Ficus sylvestris* and *F. doliaria*, Peckolt (*N. Br. Arch.* 105, 31); on a sap from Guiana, Hancock (*Ed. N. Phil. J.* 1, 240). Some other saps are described in the Appendix (p. 351).

If the exuding sap of the stem of *Ficus religiosa* be received in ether, a colourless syrup is obtained, which when diluted with more ether throws down a deposit. On evaporating the solution, the caoutchouc remains as an elastic mass, which may be freed from adhering wax by boiling with alcohol (Nesenbeck & Marquart). — The sap of *Siphonia elastica* diluted with 4 parts of water, and allowed to stand for twenty-four hours, deposits the caoutchouc in the form of a creamy layer, to be purified by repeated washing with water. This very finely divided caoutchouc, intimately mixed with water, is converted into a soft curdy mass on removing the water by evaporation or by the action of drying substances, and when further evaporated or pressed, passes into a close elastic condition, after which it is no longer miscible to a cream with water (Faraday).

The caoutchouc of commerce is made by drying successive layers of the sap on clay over a fire, or by evaporating it in the sun. It may also be obtained by allowing the sap to curdle in the air, and then removing the upper solid elastic portion from the whey beneath. — Pure caoutchouc is obtained by dissolving the crude product in chloroform and precipitating with alcohol (Adriani).

Pure caoutchouc appears white and opaque so long as it contains water between its particles, but after long drying in the air, it becomes colourless and transparent, and only slightly coloured in large masses. It possesses the elasticity of ordinary caoutchouc, has a silky lustre and a fibrous appearance when stretched, and exhibits no trace of texture (Faraday). According to Payen, however, thin sheets of crude caoutchouc exhibit irregular rounded pores, and under a magnifying power of 300 diameters a reticulated texture. See also Page (*Repert. Pat. Invent.* 1858). — Common caoutchouc is generally black outside, pale-yellow within, and opaque; the lighter cut surfaces soon turn brown on exposure to the air. Sp. gr. of pure caoutchouc = 0·925 (Faraday), of commercial 0·9335 (Brisson), of the bottle India-rubber 0·9454; of the so-called *Speckgummi* 0·9628 at 20° (Adriani), varying in different kinds between 0·919 and 0·943 (Ure). The specific gravity is not increased by pressure (Faraday). — At ordinary temperatures caoutchouc is soft, tough, and highly elastic; freshly cut surfaces remain for a long time sticky, and may be united together so that the connection is as perfect at the joint as at any other part. Below 0° it is hard, slightly flexible, no longer adhesive on freshly cut surfaces, and but slightly

elastic. It evolves heat when stretched; a string of caoutchouc by which a weight is suspended contracts when warmed and expands on cooling (Gough, *N. Gehl.* 9, 217). — Caoutchouc is a non-conductor of electricity (Faraday); and becomes highly electric when rubbed. — Has a faint odour. Tasteless. — It is not quite impervious to water, since under water it gradually absorbs the liquid and becomes opaque (Faraday). According to Chevreul and Peyron, it is not quite impermeable by gases; Berzelius, however, found the barometric pressure, under the receiver of an air pump with india-rubber joint, unchanged after twenty-four hours.

| | | | Faraday. | | Ure. | | Williams. | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Purified. | | Brown. | | Yellow. |
| 40 C ............. | 240 | .... | 88·24 | .... | 87·2 | .... | 90·00 | .... | 86·1 | .... | 87·2 |
| 32 H ............. | 32 | .... | 11·76 | .... | 12·8 | .... | 9·11 | .... | 12·3 | .... | 12·8 |
| $C^{40}H^{32}$ ........ | 272 | .... | 100·00 | .... | 100·0 | .... | 99·11 | .... | 98·4 | .... | 100·0 |

The following formulæ have been proposed for the composition of caoutchouc : $C^{9}H^{2}$ (Ure), $C^{8}H^{7}$ (Faraday ; Payen & Pelletier) $C^{12}H^{10}$ (Soubeiran). The above formula of Williams agrees with the composition of the oil of caoutchouc. — Isomeric with dammaryl and gutta-percha.

¶ Pure unmanufactured or virgin Para caoutchouc and good sheet masticated or manufactured caoutchouc were found by Miller to contain :—

| | Virgin. | | Masticated. |
|---|---|---|---|
| Pure caoutchouc ............ | 96·6 | ............ | 96·64 |
| Moisture............................ | 1·3 | ............ | 0·82 |
| Resin ................................ | 1·8 | ......... ... | 2·06 |
| Ash ..................................... | 0·3 | ............ | 0·48 |
| | 100·0 | ............ | 100·00 |

On deducting moisture and ash, the elementary composition is :—

| | Virgin. | | Masticated. |
|---|---|---|---|
| Carbon ..................... | 85·82 | ............ | 85·53 |
| Hydrogen ................. | 11·11 | ............ | 12·06 |
| Oxygen ..................... | 3·07 | ............ | 2·41 |
| | 100·00 | ............ | 100·00 | ¶ |

Crude caoutchouc contains a nearly insoluble ingredient, tough, elastic, and slightly sticky, which is the pure caoutchouc, or caoutchouc proper, together with a soluble, ductile, sticky body, fat, volatile oil, nitrogenous matters, one of which is extracted, together with the fat, by alcohol and water (Payen). It contains sulphuretted, nitrogenous, and chlorinated substances, which pass over, more or less decomposed on dry distillation (Cloez & Girard, *Compt. rend.* 50, 874).

Caoutchouc oxidises slowly at ordinary temperatures, and becomes brittle. When dried over oil of vitriol for a month, it contains 78·25 p. c. C., 11·34 H., and 11·40 O. (Adriani).

¶ 500 grains of pale-brown virgin Para caoutchouc in a narrow tape-like strip, exposed in netting in the open air to sun and rain for nine months, became blackened and rotten, but was neither sticky nor crumbled, and increased in weight 34·5 grains or 7 p. c. — Another similar piece exposed to air and light for the same time in a dry bottle placed with its mouth downwards, gained, by absorption of oxygen,

14 grains or 2·8 p. c., and became brown, soft, and sticky, especially in the parts most exposed to light. It gave up to alcohol, 11·81 p. c. of an oxidised soft viscous resin, containing 67·23 p. c. carbon, 9·34 hydrogen, and 23·23 oxygen. — A similar sample of masticated sheet caoutchouc exposed to sun and rain collected into a sticky mass which had lost its tenacity and elasticity. Another sample of the same exposed in the inverted bottle to diffused light and air, gained 8 grains or 1·6 p. c., and collected into a lump which was viscous and had lost its elasticity, especially in the parts most exposed to light. Alcohol extracted from it 12·64 p. c. of resinous matter. A third sample exposed freely to the air in a glass bottle, but kept in the dark, gained only 0·6 p. c., showed no alteration in tenacity or elasticity, and yielded to alcohol only 2 p. c. of resin (Miller). ¶

From calico which had been saturated with a solution of caoutchouc in naphtha, and had been left to itself for six years, benzene extracted a brownish-yellow resin, fusible below 100°, and containing 64·00 p. c. C., 8·46 H., and 27·54 O. The resin closely resembled shellac, dissolved in alkalis, and was precipitated from the solution by acids, and was easily soluble in alcohol, benzene, and chloroform, but insoluble in sulphide of carbon and oil of turpentine (Spiller, *Chem. Soc. J.* [2] 3, 44; *Chem. Centr.* 1865, 495).

Caoutchouc when heated in the air burns with a bright white, smoky flame, emitting a disagreeable odour. — According to Achard it melts at about 125° [160° (Himly)], giving off aromatic odours, and remains of a tarry consistence on cooling; but after longer melting, it cools to a black, brittle mass. When pure caoutchouc is gently heated in a glass tube, it volatilises in a decomposed state, leaving only a trace of charcoal (Faraday).

The products of the dry distillation of ordinary caoutchouc are carbonic acid, hydrocarbons, ammoniacal water, and empyreumatic oils, the last of which are yellow and fluid when distilled at a low temperature, but brown and thick and have a stronger smell at high temperatures (Achard). There remains a little porous charcoal, together with ash.

The empyreumatic *caoutchouc oil*, purified [from volatile bases (Williams)] by treating it with dilute sulphuric acid, water, and solid caustic potash, is a mixture of hydrocarbons of various boiling-points. By submitting it to fractional distillation, at last over sodium, the following products are obtained. 1. A very easily volatile liquid, consisting, according to Himly, of eupione (xv, 152), boiling at 33° to 44° [see on the contrary, Liebig, *Ann. Pharm.* 16, 61]; according to Bouchardat butylene (x, 66), boiling at 10°, and cautchene (x, 21), boiling at 14·5°; according to Williams *isoprene*, $C^{10}H^8$, boiling at 37° to 40°. — 2. A body boiling at 171·5°, = caoutchin (xiv, 326), $C^{20}H^{16}$. — 3. *Hevene*, or *Heveene*, the least volatile of the oils, having an amber-yellow colour, of sp. gr. 0·921 at 21°, boiling at about 315°, and remaining fluid in the cold. This body has a faint empyreumatic odour, and a harsh taste, and is without action on polarised light: it contains 86·11 p. c. C., and 14·02 H., or equal numbers of atoms of carbon and hydrogen. Hevene is inflammable and not completely volatile without decomposition: it absorbs chlorine abundantly, giving off hydrochloric acid, and is converted into a black resin. Hevene forms with oil of vitriol a viscid mass, from which there separates a colourless oil boiling at 228° (Bouchardat).

*Nitric acid* colours caoutchouc yellow, evolving nitrogen, carbonic acid, and hydrocyanic acid, and producing oxalic acid and a fatty body. Six parts of fuming nitric acid dissolve 1 part of caoutchouc completely, with effervescence, forming a dark-brown solution, from which water throws down yellow flocks, soluble in alcohol, acids, and alkalis, and inflammable at 100° (Achard). Melted caoutchouc takes fire when strong nitric acid is poured upon it (Hare). When digested for 12 hours with nitric acid, caoutchouc is converted into a soft, yellow, non-elastic mass (Roxburgh). Caoutchouc is dissolved by boiling nitric acid of sp. gr. 1·35, without any violent action, forming camphretic acid and a small quantity of resin precipitable by water (Schwanert, *Ann. Pharm.* 128, 123). — *Oil of vitriol* converts moderately thin pieces of caoutchouc, after some days only, into a black friable substance without dissolving it (Roxburgh): when heated, it produces a turpentine-like mass, from which water separates a black brittle resin (Achard). — The dark-brown solution of caoutchouc in bisulphide of carbon is decolorised by passing chlorine-gas into it, and on subsequent addition of water, deposits a white, non-elastic mass. Sulphurous acid acts in the same manner (Traun). — When thrown upon melted *chlorate of potash*, caoutchouc burns with a very bright flame, evolving a large quantity of heat, so that the bottom of the glass tube containing it is melted (Böttger, *N. Repert.* 6, 247).

*Combinations.* Caoutchouc does not dissolve in *water* at any temperature, but swells up and becomes sticky in boiling water ; after cooling it remains softer and more bulky than before, and is found to have taken up water. Thin strips of caoutchouc kept in water for 30 days take up from 18·7 to 26·4 p. c., and increase in length and thickness (Payen). Boiling water sometimes takes up a little resin from commercial caoutchouc.

¶ A narrow strip of virgin Para caoutchouc, weighing 500 grains, exposed to diffused light in fresh water in an open bottle, became white and opaque from absorption of moisture, and increased by 86 grains, or 17 per cent., but experienced no other alteration in chemical properties, and resumed its original characters when dried. A similar sample exposed in sea-water, in an open bottle to diffused light, absorbed 3·6 per cent. of its weight of water, but was only a little altered in appearance, not in chemical composition. A sheet of masticated caoutchouc immersed in fresh water, open to the air and diffused light, increased 87 per cent. by absorption of water, that is to say, it nearly doubled its weight. It became white, opaque, slimy, and sticky when pressed, and allowed water to be squeezed out by pressure. It lost weight rapidly by drying when exposed to the air. — Another sample similar to the last, but exposed in sea-water, became slightly opaque and slimy, but increased only 5 per cent. in weight by absorption. A second sample, in sea-water in a closed bottle, emitted a smell of sulphuretted hydrogen, and gained 5·6 per cent. in weight by absorption. Its elasticity and tenacity were not impaired. A quantity of acetate of potash having been enclosed in bags made of sheet rubber and accurately sealed, and the bags immersed in water, the salt in each of the bags was found at the end of nine months to have become liquefied by the water which it had absorbed, and the bags had in each case gained in weight several grains (Miller). ¶

Caoutchouc is insoluble in aqueous *hydrochloric acid*, and is not acted

upon by dilute *sulphuric acid*. — Aqueous *potash*, even in very strong solution (Faraday), and alcoholic potash are without action on caoutchouc, even when heated (Bernard; Achard). Contrary to Thorey and Thomson, who found it softened and dissolved thereby. — Caoutchouc is not acted on by *ammonia-gas*: when digested for some months in solution of ammonia, it colours the liquid brown, assumes a silky lustre, and swells up, and when shaken with oil of turpentine, dissolves to an emulsion, from which the greater part of the caoutchouc separates in the form of a cream on standing (*Ann. Pharm.* 23, 359). See also Sumers (*Dingl.* 64, 77; 69, 158). — Caoutchouc is apparently not altered in liquid *carbonic acid*, but when taken out of the liquid, it swells up to six or eight times its volume and afterwards contracts again, having become white throughout the entire mass (Gore, *Rép. Chim. pure*, 3, 214).

By contact with *sulphur*, under favourable conditions, caoutchouc is converted into *vulcanised caoutchouc*, further into *vulcanised caoutchouc less rich in sulphur*, and *hardened caoutchouc*.

*a.* When sheets of caoutchouc, 2 or 3 millimetres thick, are immersed for two or three hours in melted sulphur, at a temperature of 112° to 116°, the sulphur permeates the pores of the caoutchouc more quickly than water or alcohol would do, and increases its weight from 10 to 15 p. c. without altering its behaviour towards solvents. If it be now heated from 135° to 160° for a few minutes, combination with the sulphur takes place and it is converted into vulcanised caoutchouc. Hancock's process (*Lond. Journal of Arts*, 1845, 178).

Vulcanised caoutchouc remains equally elastic and soft at temperatures varying between $-20°$ and $+50°$, and does not soften to any great extent even at 100° or higher. — Under water it takes up a much smaller quantity of the liquid than crude caoutchouc, and permits the evaporation of water from vessels made of it to a much less extent. The combination with sulphur does not alter the proportion of carbon to hydrogen, which corresponds, as in crude caoutchouc, to the formula $C^8H^7$ (Payen). Vulcanised caoutchouc is much less easily attacked by solvents than crude caoutchouc; but, according to Baumhauer, it is rendered porous by the action of ozone.

¶ Miller found that a sheet of vulcanised caoutchouc exposed in netting to the sun and rain, lost 2 p. c. in weight, and was scarcely less tenacious than at first. A similar sheet immersed in fresh water absorbed 19 p. c., but was not otherwise altered. A similar sheet in sea-water became rather more slimy, but gained only 1·6 p. c. in weight. ¶

Vulcanised caoutchouc may also be obtained by mixing crude caoutchouc with finely-powdered sulphur and heating to 135° to 160° (Goodyear's method), and probably also by kneading it with sulphide of lead or mineral kermes. It is formed by dipping crude caoutchouc into a mixture of bisulphide of carbon and chloride of sulphur (Parkes), or by heating it to 140° for some hours with polysulphide of potassium (Gerard).

*b.* Vulcanised caoutchouc contains 1 to 2 per cent. of combined sulphur, the remainder being enclosed mechanically in the pores. This excess is gradually separated by the stretching and contracting of the caoutchouc during some months, and may be more quickly and completely removed by means of hot caustic potash. The caoutchouc less rich in sulphur thus obtained still retains its elasticity at various temperatures and its indifference towards solvents.

*c.* When subjected to prolonged heating, especially in melted sulphur,

vulcanised caoutchouc becomes hard and horny, and susceptible of polish, these properties increasing with the proportion of sulphur and the duration of heating. Hydrosulphuric acid is evolved in the reaction, especially when the temperature exceeds 160°, part of the gas remaining dissolved in the excess of sulphur and escaping only as the sulphur crystallises. Goodyear heats 1 part of caoutchouc with ⅓ part of sulphur to 100° for 2 hours, and afterwards to 151° for 4 hours. Hardened caoutchouc is still less soluble than the vulcanised, and scarcely swells even in bisulphide of carbon. Ebermayer found in the hardened caoutchouc of commerce 12 to 28 p. c. of sulphur.

Caoutchouc dissolves partially in *bisulphide of carbon* (Lampadius). It swells up in that liquid to a spongy mixture of a dissolved and an undissolved body, and dissolves to the extent of 30 to 70 per cent. (Payen). Caoutchouc in pieces, digested with six parts of bisulphide of carbon, swells up over night to a soft unctuous mass (Dullo). The solution may be accelerated by agitation with shot (Anthon, *Repert.* 52, 372). If the bisulphide contains free sulphur, the caoutchouc takes up that body and remains as vulcanised caoutchouc on evaporation (Dullo).

Caoutchouc swells up in cold, and still more in boiling *alcohol*, without dissolving. Boiling alcohol takes up from crude caoutchouc a bitter, sticky resin, amounting in some cases to 4 p. c. (Adriani); sometimes also a little wax (Nesenbeck). Thin sheets of caoutchouc become opaque and sticky by absorption of alcohol (Payen). — Anhydrous *ether* decomposes caoutchouc in the same manner as bisulphide of carbon, forming a colourless solution and leaving 34 p. c. of a coloured substance undissolved (Payen). Macquer found it completely soluble; Berniard and Roxburgh quite insoluble, in ether. Pure caoutchouc swells up very much in ether, but dissolves very slightly (Nees v. Esenbeck and Marquart). The addition of a little sulphuric acid (van Gears, *Repert.* 52, 392), or previous boiling with water (Stratingh), greatly promotes the solubility in ether. The presence of alcohol in the ether prevents the swelling of india-rubber bags (Mohr, *Ann. Pharm.* 22, 184), though according to Payen, caoutchouc swells to 4 times its volume in a mixture of 1 volume of absolute alcohol and 6 volumes of ether. — The solution in ether is precipitated by alcohol; it leaves unchanged caoutchouc on evaporation. See also Juch. (*A. Gehl.* 4, 226); Pfaff (*Schw.* 61, 384). A mixture of 100 pts. bisulphide of carbon and 6 or 8 pts. absolute alcohol dissolves caoutchouc very easily: when one volume of the solution is mixed with 2 vols. absolute alcohol, the whole of the caoutchouc is precipitated, whilst fat and colouring matter remain in solution. The viscid precipitate, saturated with bisulphide and alcohol, dissolves easily in a larger quantity of bisulphide to a clear liquid (Payen). Caoutchouc swells up in *chloride of ethyl* and *nitric ether*, turning white and dissolving (Achard; Pfaff, *N. Gehl.* 5, 335). It is scarcely soluble in *acetone* (Wiederhold), but swells up therein to a jelly (Trommsdorff).

Caoutchouc dissolves in *chloroform* much more easily than in other liquids, and remains unchanged on evaporating the solution (Cloez, *N. J. Pharm.* 14, 382). Solution is effected only on triturating the jelly first formed. Alcohol precipitates the caoutchouc in a coherent, elastic mass (Schwerdtfeger, *N. Jahrb. Pharm.* 1, 100). When pieces of caoutchouc are heated to 100° in a sealed tube, with more than twice their bulk of chloroform, a jelly is produced which is fluid when

heated, and mixes with bisulphide of carbon without precipitation (Traun).

Caoutchouc swells up in *fusel oil, amyl-aldehyde, valerianate of amyl,* and *valerianic acid* (Trautwein, *Repert.* 91, 29).

Caoutchouc swells up very much in the *rectified empyreumatic oils of caoutchouc* (xiv, 326) in the *light oils of coal-tar, rock oil, oil of turpentine freed from resin and rectified,* in the *light resin-oils, eupione, oil of cajeput, oil of lavender,* and in many other *volatile oils,* dissolving in these liquids in the same manner as in ether. It does not swell in *creosote,* and softens only on long boiling therein, without dissolving (Reichenbach). *Fatty oils* also, and *hog's lard* and *spermaceti* dissolve caoutchouc on heating, or mix with it when melted. See Reichenbach (*J. pr. Chem.* 1, 388), Märker (*Jahrb. pr. Pharm.* 2, 226), Mohr (*Ann. Pharm.* 21, 342; 22, 184), Martin (*Ann. Pharm.* 22, 99), Roxburgh (*Repert.* 35, 349), Dullo (*Polyt. Notizbl.* 20, 90).

¶ Virgin Para caoutchouc resists the action of *linseed oil,* whether *boiled* or *unboiled,* and of *Stockholm tar* almost perfectly, retaining its toughness, excepting in those parts which are above the surface of the liquid and exposed to light. In the tar it contracts spontaneously, but still remains strong and elastic. — Masticated caoutchouc, exposed to the action of the same liquids, becomes greatly swollen and gelatinized, and in the case of the unboiled oil is completely dissolved. Vulcanized caoutchouc similarly treated loses its tenacity, and becomes swollen and gelatinous, but retains its form and a certain degree of elasticity (Miller). ¶

### Appendix to Caoutchouc.

1. *Milky sap of Tabernamontana utilis, from Guiana.* — Contains water, sugar, gum, salts, a resin melting at 170° and brittle at 160°, and represented by the formula $C^{30}H^{24}O^2$ (81·47 p. c. C., 11·14 H., 7.39 O), a second resin melting at 140° to 150°, and softening at 60°, represented by the formula $C^{30}H^{26}O^2$ (81·22 p. c. C., 11·51 H., 7·27 O.), and caoutchouc. To obtain this last substance, the sap is curdled by alcohol, and the curdled mass is washed and exhausted with cold and boiling absolute alcohol in succession, whereby the resins are dissolved, and the caoutchouc left behind. It is elastic, soluble in boiling ether to a milky liquid, and contains 82·85 p. c. C., 11·68 H., and 5·47 O, corresponding to the formula $C^{40}H^{34}O^2$ (Heintz, *Pogg.* 65, 260). To this place belongs also a sap investigated by Marchand (*J. pr. Chem.* 21,48) as the milk of the cow-tree, in which he found two resins, together with caoutchouc containing 81·10 p. c. C., 11·02 H., and 7·98 O., corresponding to the formula $C^{40}H^{33}O^3$. See also Christison (*Ed. N. Phil. J.* 9, 32).

2. *Resins from the milk of the Cow-tree (Galactodendron utile).* The milk preserved by addition of alcohol contains a resin soluble in cold and in boiling alcohol, and very easily also in ether, not decomposible by digestion with strong caustic potash, and not precipitable by alcoholic neutral acetate of lead or nitrate of silver. It contains, on the average, 82·27 p. c. C., 11·40 H., and 6·33 O., corresponding to the formula $C^{70}H^{58}O^4$, and forms 31·4 p. c. of the milk. — The milk imported

without addition of alcohol contains altered resins (Heintz, *Pogg.* 65, 240). See also Boussingault & Rivero (*Ann. Chim. Phys.* 23, 219), Solly (*Phil. Mag.* 11, 452).

3. *Resin from the milk of Hura crepitans,* a Brazilian tree. — The yellowish inodorous, milky sap, tastes weak at first, but afterwards extremely irritating in the throat; its vapour produces violent inflammation. — On boiling with alcohol the sap evaporated to an extract, evaporating the filtrate, and exhausting the residue, first with boiling water and then with ether, the ether takes up resin and leaves undissolved an oil, which, when freed from adhering ether by evaporation, solidifies to a crystalline mass, having a burning, acrid taste, and the property of reddening turmeric. —The resin is yellow, sticky, inodorous, tasteless at first, but afterwards acrid; it produces blisters on the skin. At a little over 100° it is fluid, and boils and volatilises undecomposed in open vessels, more especially with vapour of water or alcohol; the vapours blister the face and cause inflammation. It is easily soluble in alcohol, ether, and oil of turpentine, but nearly insoluble in aqueous ammonia or potash (Boussingault & Rivero, *Ann. Chim. Phys.* 28, 430; *Repert.* 23, 189). See also Merat & Gilbert (*Pharm. Centr.* 1849, 30).

4. *Chinese India-rubber.* — Probably formed by the desiccation of drying oil. Yellow (also red or blue); slightly elastic; lighter than water. Burns with a bright flame, even on water, leaving a little ash. Softens when boiled with water, and melts to a black, brittle mass when heated. Dissolves completely in warm aqueous carbonate of potash, forming a soap. Alcohol takes up a portion when warmed with it, and leaves the rest in the form of a white mass. It is insoluble in volatile oils (Thorey, *Crell. Chem. J.* 2, 107.)

## 5. Viscin.

P. Reinsch. *N. J. Pharm.* 14, 129; abstr. *Chem. Centr.* 1861, 145; *Kopp's Jahresber.* 1860, 541.

The white, semi-elastic substance, extremely sticky and viscid when warmed, which exudes from the disc and floral envelopes of *Atractylis gummifera,* was termed viscin by Macaire-Princep (*Bibl. univ.* 54, 19; *J. pr. Chem.* 1, 415; *Ann. Pharm.* 12, 261), and recognised by him as identical with the essential constituent of bird-lime. It is insoluble in water and alcohol, but dissolves in ether and oil of turpentine, and remains sticky and viscid on evaporating the solution, without drying up in the air. Macaire's supposition that this viscin does not exist in the fresh berries and husks of the mistletoe, or in the bark of holly, but is produced only in the process of making bird-lime, appears to be erroneous.

*Bird-lime* is obtained from the bark, leaves, or berries of mistletoe (*Viscum album*) by boiling, or better by crushing and washing with water. Or the inner peel of the twigs of *Ilex aquifolium* is cut in pieces and softened by boiling with water, and then buried in the earth in a closed vessel and allowed to remain for some weeks, after which the mass may be kneaded into a semi-transparent green paste.

The same or similar substances occur in the epidermis of young twigs of *Robinia viscosa* (Vauquelin, *Scher. J.* 3, 120), in the bark of *Ilex aquifolium* (Bouillon Lagrange; Henry, *N. Tr.* 3, 2, 289), in the root of *Gentiana lutea*, together with soft resin (N. E. Henry, *J. Pharm.* 5, 97; 7, 175; Leconte, *J. Pharm.* 23, 474), in the sticky coatings of *Lychnis Viscaria* and *Saxifraga tridactylites*. — The sap of the young twigs of *Ficus elastica*, and of other species of *Ficus*, contains viscin, in the form of a white body, which may be drawn out in long threads, and is insoluble in alcohol, but soluble in ether; the sap of the stem, however, contains caoutchouc (Nees v. Esenbeck & Marquart, *Ann. Pharm.* 14, 43). Concerning the viscin of *Atractilis*, see also Geiger (*Mag. Pharm.* 24, 23), Landerer (*Repert.* 63, 192).

*Preparation.* Bird-lime is prepared from the white berries of the mistletoe by grinding them with water and straining off the skins, or from the finely-scraped bark by kneading it with water till all soluble matters are removed, and a mixture of bird-lime and woody fibre remains. This mass is kept under water for some days, the water being frequently renewed, and is then digested with 90 p. c. alcohol so long as it colours that liquid yellow, after which it is boiled repeatedly with alcohol, whereby wax is removed. The remaining yellowish-brown mass, when treated five or six times with ether, gives up viscin, whilst viscaoutchin and woody fibre remain undissolved. The ethereal solution is evaporated; the residue is warmed to drive off the last portions of ether; and the viscid yellowish mass is kneaded with alcohol so long as it gives off colouring matter. It is then kneaded under water, and heated to 120°, without access of air, till the whole of the water is expelled (Reinsch).

*Properties.* Clear transparent mass, of the consistence of honey at ordinary temperatures, and capable of being drawn out into long threads; fluid at 100°, like oil of almonds. Produces a greasy stain on paper. Sp. gr. = 1. Nearly inodorous and tasteless. Has an acid reaction.

|  |  |  |  |  | Reinsch. mean. |
|---|---|---|---|---|---|
| 40 C | 240 | ............ | 57·69 | ............ | 57·52 |
| 48 H | 48 | ............ | 11·54 | ............ | 11·52 |
| 16 O | 128 | ............ | 30·77 | ............ | 30·96 |
| $C^{40}H^{48}O^{16}$ | 416 | ............ | 100·00 | ............ | 100·00 |

Reinsch's formula is $C^{20}H^{23}O^8$; from that given above, viscin may be regarded as a hydrate of caoutchouc (Kr.).

Viscin begins to boil at 210°, and yields at 235° a thin yellow oil, Reinsch's *viscene*, of sp. gr. 0·856, boiling at 227—229°; and at temperatures gradually rising to 275°, a buttery distillate, whilst a little carbon remains behind. On shaking the distillate with caustic soda, it solidifies to a crystalline pulp, from which an oil is volatilised by boiling; the remaining soda-salt, distilled with phosphoric acid, yields the acid (Reinsch's *viscic acid*), though with difficulty, in the form of a yellow acid oil, the soda-salt of which is soluble in alcohol, but insoluble in water (Reinsch).

*Viscaoutchin* This substance remains behind, together with woody

fibre, after the extraction of viscin by ether as above, and is taken up by oil of turpentine. After distilling off the turpentine, the yellowish mass is dissolved in ether, in which it has now become soluble; the ethereal solution is evaporated; and the residue is washed with alcohol and water, and dried at 120°. — At ordinary temperatures it is viscid, and resembles vegetable wax; at 120° it is of the consistence of olive oil. Very elastic, and may be drawn out into long threads. Sp. gr. = 0·978. Tasteless; of faint odour and neutral reaction. Contains, on the average, 75·56 p. c. C., 11·91 H., and 12·53 O., corresponding to the formula $C^8H^8O$ (Reinsch). $C^{40}H^{37}O^5 = C^{40}H^{32},5HO$ requires 75·71 p. c. C., and 11·67 H. (Kr.).

*Primary Nucleus* $C^{40}H^{34}$; *Oxygen-nucleus* $C^{40}H^{28}O^6$.

## Wormwood-bitter or Absynthiin.

$$? \; C^{40}H^{28}O^8 = C^{40}H^{28}O^6,O^2.$$
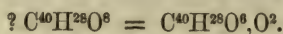
LEONARDI. *Br. Arch.* 28, 211. — Caventou. *Br. Arch.* 29, 157.
MEIN. *Ann. Pharm.* 8, 61.
RIGHINI. *J. Chim. méd.* 19, 383.
LUCK. *Ann. Pharm.* 54, 112; 78, 87.
KROMAYER. *N. Br. Arch.* 108, 129; *Chem. Centr.* 1862, 49; *Kopp's Jahresber.* 1861, 745.

The bitter principle of *Artemisia Absynthium* (Handbuch, viii, [2], 67). Investigated chiefly by Mein, Luck, and Kromayer, but with somewhat discordant results.

Frickhinger (*Repert.* 101, 365) and Landerer (*Repert.* 105, 316) described crystals deposited from *Tinctura Absynthii* on standing. — Braconnot's *absynthic acid* (*J. Phys.* 84, 341) is, according to Zwenger (*Ann. Pharm.* 48, 122), succinic acid; Tichanowitsch also found the latter acid, but Luck denies its existence in wormwood. Mein's wormwood-bitter may likewise, according to Zwenger, be succinic acid with adhering bitter substance; the properties of the body, however, do not accord with such a supposition (Kr.).

a. *According to Mein.* — Freshly dried flowering twigs of wormwood are digested in warm water, and after standing for twenty-four hours, pressed, and again treated once or twice in the same manner.

The infusions are filtered and evaporated to an extract, which is exhausted with alcohol of 36° B.; the alcohol is distilled off; the residue is again evaporated; and the portion soluble in water is separated. The undissolved portion is freed from adhering extractive by dissolving it in 3 parts of alcohol and precipitating the filtrate by water, and this process is repeated until the filtrate is no longer coloured green by sesquichloride of iron. The resinous bitter principle thus obtained resembles jalap-resin, and has an acid reaction and very bitter taste. When its solution in 24 parts of alcohol of 80 p. c. is shaken up with 96 parts of 30 p. c. alcohol, filtered after twenty-four hours from the flocks which are deposited, precipitated with neutral acetate of lead, mixed with water, and heated till the whole of the

alcohol is driven off, and the aqueous liquid filtered, freed from lead by hydrosulphuric acid, and concentrated at 60°, the liquid becomes covered with a colourless pellicle and deposits small white prisms. These prisms, which Mein regards as pure absynthiin, and classes with the crystalline resins, colour oil of vitriol an intense yellow, gradually changing to dark purple. They dissolve in 1,000 parts of water, forming a solution which reddens litmus and is precipitated by tincture of galls, but not by metallic salts. They dissolve in dilute caustic alkalis and their carbonates, and easily in acetic acid, from which they are precipitated by water; they are most easily soluble in alcohol and less freely in ether (Mein). According to Geiger, this absynthiin is a substance closely related to santonin.

b. *According to Luck.* — An alcoholic tincture of the dried herb is evaporated to a syrup, from which the wormwood-bitter and acid resin are extracted by repeated shaking with ether. The ethereal solution is distilled, and the residue treated with ammoniacal water, which takes up resin and leaves the bitter for the most part undissolved, in the form of a powder. This powder is digested with dilute hydrochloric acid to remove ammonia, washed with water, dissolved in alcohol, and precipitated with neutral acetate of lead. The filtrate is freed from lead by hydrosulphuric acid, mixed with a little water, and evaporated in a warm place, whereupon the bitter is deposited in yellow resinous drops, which become crystalline after some days or weeks. They are acid and very bitter, slightly soluble in cold, and fusible in boiling water. The red-yellow solution in cold oil of vitriol quickly turns indigo-blue in the air and then yields with water, greyish green not bitter flocks, whilst the solution remains of a rose-red colour. The solution in hydrochloric acid is yellow, but when slightly warmed, becomes red and deposits brown clots. The bitter dissolves slightly in ammonia with wine-yellow colour, and more easily in potash, forming a golden-yellow solution. When an alcoholic solution is mixed with caustic potash and treated with carbonic acid so long as carbonate of potash is deposited, the filtrate yields, with neutral acetate of lead, fine yellow flocks of absynthiin and lead-oxide, which, after a few minutes, turn white and undergo decomposition. To obtain the lead-compound, Luck mixes the alcoholic solution of the bitter with ammonia and basic acetate of lead, evaporates in a vacuum over oil of vitriol, triturates the residue and washes it with water, ether, and alcohol. Thus obtained it contains 55·25 p. c. of oxide of lead. — This wormwood-bitter dissolves easily in alcohol, less freely in ether, and also in acetic acid, from which it is precipitated by water. After drying in a vacuum, it has the following composition :—

|  | | | | | Luck. mean. |
| Calculation, according to Ludwig. | | | | | |
| 40 C | 240 | ........ | 65·93 | ........ | 65·18 |
| 28 H | 28 | ........ | 7·69 | ........ | 7·62 |
| 12 O | 96 | ........ | 26·38 | ........ | 27·20 |
| $C^{40}H^{28}O^{12}$ | 364 | ........ | 100·00 | ........ | 100·00 |

According to Luck, $C^{16}H^{11}O^5$. According to Ludwig's formula, Luck's absynthiin contains 4 at. of oxygen more than Kromayer's.

c. *According to Kromayer.* — An infusion of wormwood prepared with hot water is precipitated with infusion of galls, and the precipitate is

collected, washed, and decomposed while still moist by desiccation with oxide of lead. From the dry mass alcohol takes up the absynthiin, which is purified by treating its hot alcoholic solution with animal charcoal, and afterwards dissolving it in ether. — Or, instead of the infusion, the sap of the fresh plant, previously freed from albumin by heating, may be employed. The absynthiin thus obtained may be purified by precipitating an aqueous solution with basic acetate of lead, and removing the lead which remains in solution by hydrosulphuric acid. — On agitating an aqueous extract of the herb with animal charcoal, the absynthiin is taken up thereby, and may be extracted by alcohol, but still requires purification. Righini had previously obtained wormwood-bitter by the same process.

*Properties.* Absynthiin is obtained by the slow evaporation of its alcoholic solution, in faintly-yellow, oily drops, which solidify to a hard, indistinctly crystalline mass. The ethereal solution leaves a nearly colourless, transparent mass, triturable to a powder, which is permanent in the air. Neutral. Has an aromatic odour and very bitter taste. Melts at 120° to 125°. Free from nitrogen.

| | | *Over oil of vitriol.* | | *Kromayer.* |
|---|---|---|---|---|
| 40 C | 240 | ........ | 70·38 | ........ 70·47 |
| 29 H | 29 | ........ | 8·50 | ........ 8·78 |
| 9 O | 72 | ........ | 21·12 | ........ 20·75 |
| C⁴⁰H²⁸O⁸,HO ? | 341 | ........ | 100·00 | ........ 100·00 |

The above is the formula given by Ludwig & Kromayer, which, however, derives but little support from the analysis of tannate of absynthiin (Kr.).

*Decompositions.* 1. Absynthiin decomposes when *heated*, emitting acrid, irritating vapours. — 2. It reduces the metal from *ammoniacal nitrate of silver.* — 3. It is decomposed by *nitric acid* only when hot. — 4. The brown solution in *oil of vitriol* quickly turns greenish-blue, or when water is dropped into it, dark-blue; with a larger quantity of water it deposits grey flocks. Dilute *sulphuric* and strong *hydrochloric acids* produce brown resins, but no sugar. — Absynthiin does not reduce an *alkaline solution of cupric oxide.*

Absynthiin is nearly insoluble in cold, and but slightly soluble in hot *water*; the excess melts in the liquid to transparent oily drops. The solution does not precipitate *metallic salts.*

Absynthiin dissolves in *caustic potash,* with brown-red colour, and is not precipitated from the solution by hydrochloric acid. Hydrochloric acid throws down part of the absynthiin from its solution in aqueous ammonia, the precipitate dissolving in excess of the acid with rose-red colour.

*Tannate of Absynthiin.* — Alcoholic absynthiin, to which water is added till cloudiness is produced, forms with aqueous tannic acid a white, plaster-like precipitate, which, after washing with water and weak alcohol and drying at 100°, may be triturated to a grey powder.

| *Calc. according to Ludwig & Kromayer.* | | | | Kromayer. at 100°. |
|---|---|---|---|---|
| 58 C | 348 | ........ | 60·94 | ........ 61·03 |
| 39 H | 39 | ........ | 6·83 | ........ 7·20 |
| 23 O | 184 | ........ | 32·23 | ........ 31·77 |
| C⁴⁰H²⁸O⁸,C¹⁸H⁸O¹² + 3HO ? | 571 | ........ | 100·00 | ........ 100·00 |

Absynthiin dissolves easily in *alcohol* and *ether*.

When the alcoholic tincture of wormwood is precipitated with alcoholic neutral acetate of lead, and the precipitate is dried, triturated, and washed with water, acetate and succinate of lead are dissolved. From the dried residue, ether takes up *resin of wormwood* and a little wormwood-bitter, the latter of which is removed by repeated boiling with water. The resin is yellowish, scarcely acid in alcoholic solution, and fusible in water to an oil, which floats on the surface. It dissolves in oil of vitriol, from which it is precipitated by ammonia, and is easily soluble also in boiling caustic potash and in ammonia, whereupon excess of ammonia throws down a precipitate. It does not affect acetate of copper or nitrate of silver, and dissolves easily in alcohol and ether (Tichanowitsch, *Zeitschr. Ch. Pharm.* **6**, 197 ; *Chem. Centr.* 1863, 908).

Oxygen-nucleus $C^{40}H^{26}O^{8}$.

# Asarone.

$$C^{40}H^{26}O^{10} = C^{40}H^{26}O^{8}, O^{2}.$$

Görz. *Pfaff's System der Materia med.* 3, 229.
Lassaigne & Feneulle. *J. Pharm.* 6, 561 ; *N. Tr.* 5, 2, 72.
Gräger. *Dissert. de Asara europ. Göttingen* 1830.
Sell & Blanchet. *Ann. Pharm.* 6, 296.
K. Schmidt. *Ann. Pharm.* 53, 156 ; *J. pr. Chem.* 33, 221.

*Asarabacca-camphor. Haselwurz-campher.* — Discovered by Görz. — Occurs in the root of *Asarum europæum*, which, according to Lassaigne & Feneulle, contains also a bitter substance. Gräger further distinguishes as *Asarite*, crystals obtained in the same way as asarabacca-camphor, and apparently identical therewith.

*Preparation.* When the dried root is distilled with 8 parts of water till 3 parts have passed over, one portion of the asarone collects in white granules in the neck of the retort and below the distillate, while another portion is deposited from the distillate in the cold (Görz). Gräger purifies the product by dissolving it in alcohol and precipitating with water, and frees it from admixed asarum-oil (xiv, 359) by fusion.

*Properties.* Transparent, pearly, four-sided tables (Lassaigne & Feneulle). Crystals of the oblique prismatic system, occurring in various forms (Schmidt). See the description (*loc. cit.*). Sp. gr. = 0·95 (Gräger). Melts at 40° (Blanchet & Sell), 70° (Gräger), and solidifies at 27° (Blanchet & Sell) in a radiated crystalline mass. Sublimes in small quantities between two watch-glasses, but a portion is easily rendered brown and empyreumatic. The strongly smelling vapour excites coughing. — Inodorous and tasteless (Gräger); according to Görz it smells and tastes like camphor and acts as an emetic.

|  |  |  |  |  | Blanchet & Sell. mean. | | Schmidt. mean. |
|---|---|---|---|---|---|---|---|
| 40 C | 240 | ........ | 69·37 | ........ | 68·66 | ........ | 69·37 |
| 26 H | 26 | ........ | 7·51 | ........ | 7·74 | ........ | 7·66 |
| 10 O | 80 | ........ | 23·12 | ........ | 23·60 | ........ | 22·97 |
| $C^{40}H^{26}O^{10}$ | 346 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

According to Blanchet & Sell, $C^{16}H^{11}O^4$; according to Schmidt $C^{20}H^{13}O^5$.

*Decompositions.* 1. When asarone is *heated* above 100° in a sealed glass tube, the fused mass crystallises on cooling the more slowly in proportion as it has been longer and more strongly heated ; if heated to 210° for half an hour, it crystallises completely only after three days (Schmidt). — 2. It begins to *boil* at 280°, but decomposes without distilling, the temperature rising to 300° (Blanchet & Sell): the residue forms a red viscid mass, from which the asarone crystallises after some days (Schmidt). — 3. The easily formed solution of asarone in strong warm alcohol, when boiled for 10 or 15 minutes, assumes at last a deep blood-red colour and deposits only a part of the asarone in crystals on cooling, the mother-liquor drying up to a red, tough resin, which carbonises without subliming when heated, and is precipitated from its alcoholic solution by water in amorphous globules, containing 69·03 p. c. C., 7·65 H., and 23·32 O. This resin (amorphous *asarone*) yields the original crystals when distilled with water (Schmidt). — 4. Asarone *burns* with a bright smoky flame (Gräger). — 5. It dissolves in strong *nitric acid*, forming oxalic acid (Schmidt), and leaving a tough yellow resin (Görz). — 6. When heated with *bichromate of potash and sulphuric acid* it yields an amorphous red resin, neutral, precipitable from its alcoholic solution by water, and containing 66·0 p. c. C., 6·89 H., and 27·11 O. Oxide of manganese and sulphuric acid act in a similar manner, but the resin is not altered by peroxide of lead or by melting in hydrochloric or sulphurous acid gases (Schmidt). — The crystals do not melt in the vapour of *anhydrous sulphuric acid*, and are only partially attacked, the edges assuming red, black, and other colours. A conjugated compound of sulphuric acid appears to be formed (Schmidt). — The crystals dissolve in cold *oil of vitriol* with yellow, and in the hot liquid with brown-red colour : from the former solution water throws down unchanged asarone, from the latter a brown resin (Gräger ; Schmidt). — 8. Asarone is not attacked by *chlorine* in a freezing mixture, but at ordinary temperatures it melts, with considerable evolution of heat, to a deep blood-red mass, which afterwards gives off hydrochloric acid and turns green, and then absorbs chlorine quietly. When 100 parts of asarone have taken up 46 parts of chlorine, the green, non-volatile, resinous residue contains 47·16 p. c. C. and 4·41 H., and has, therefore, exchanged hydrogen for chlorine (Schmidt).

Asarone dissolves slightly in hot *water* (Görz), and easily in *alcohol*, precipitable therefrom by water in the form of an oil, which crystallises. It dissolves in *ether* and *volatile oils* (Gräger).

*Oxynitroazo-nucleus* $C^{40}N^2X^2H^{20}O^{10}$.

# Cacotheline.

$$C^{40}N^4H^{22}O^{16} = C^{40}N^2X^2H^{20}O^{10},H^2.$$
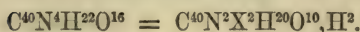
GERHARDT. *Compt. rend.* 19, 1105 ; *Compt. chim.* 1845, 112 ; *J. pr. Chem.* 36, 11. — *N. J. Pharm.* 9, 317 ; 13, 232 and 14, 212.
LAURENT. *Compt. rend.* 22, 633 ; *N. Ann. Chim. Phys.* 22, 463 ; *J. pr.*

*Chem.* 45, 378. — *N. Ann. Chim. Phys.* 24, 314; *Ann. Pharm.* 69, 15; *J. pr. Chem.* 46, 32.

ROSENGARTEN. *Ann. Pharm.* 65, 111; *Pharm. Centr.* 1848, 199; *N. J. Pharm.* 13, 232; *Kopp's Jahresber.* 1847—48, p. 632.

A. STRECKER. *Ann. Pharm.* 91, 76; *J. pr. Chem.* 62, 437; *Pharm. Centr.* 1854, 652; *Compt. rend.* 39, 54; *N. Ann. Chim. Phys.* 42, 366; *Kopp's Jahresber.* 1854, 520.

*Kakothelin.* Discovered by Gerhardt and Laurent; investigated chiefly by Strecker. — Formed, together with nitrite of methyl, carbonic acid, and oxalic acid, by the action of nitric acid on brucine (See BRUCINE).

*Preparation.* When nitric acid of sp. gr. 1·4 is poured upon melted brucine in a retort, a violent action occurs, attended with evolution of gases and red vapours: if necessary, the retort may be placed in cold water to moderate the action. The contents of the retort are diluted with water, and the precipitated yellow flocks are collected and washed with water. The mother-liquor, when concentrated, freed from crystals of oxalic acid, and diluted with water, yields an additional quantity of the product. The flocks may be crystallised from water containing nitric or hydrochloric acid (Strecker).

*Properties.* The yellow or orange-yellow crystals lose their water at 100°, becoming at the same time darker in colour if they have been crystallised from hydrochloric acid (Strecker). They assume a dark-brown colour in sunlight (Laurent), and explode when heated (Gerhardt).

|  |  |  | Laurent. mean. |  | Rosengarten. mean. |  | Strecker. mean. |
|---|---|---|---|---|---|---|---|
| 40 C | 240 | ........ | 51·95 | ........ | 51·34 | ........ 51·67 | ........ | 52·1 |
| 4 N | 56 | ........ | 12·12 | ........ | 11·20 | ........ 12·70 | ........ | 12·6 |
| 22 H | 22 | ........ | 4·76 | ........ | 4·40 | ........ 5·06 | ........ | 4·9 |
| 18 O | 144 | ........ | 31·17 | ........ | 33·06 | ........ 30·57 | ........ | 30·4 |
| $C^{40}N^2X^2H^{22}O^{10}$ | 462 | ........ | 100·00 | ........ | 100·00 | ........ 100·00 | ........ | 100·0 |

The above is Strecker's formula: Laurent proposed $C^{42}N^4H^{22}O^{20}$. For Stahl-schmidt's views on the formula of cathoteline, see *Pogg.* 108, 542.

*Combinations.* A. *With Water.* — Cacotheline crystallised from water containing nitric acid lost 4·1 p. c. of water at 100° (2 at. = 3·8 p. c.), but when crystallised from water containing hydrochloric acid, it lost 1·9 p. c. (1 at. = 1·9 p. c. HO) (Strecker).

Cacotheline is nearly insoluble in water, either cold or boiling.

B. *With Acids.* — Cacotheline dissolves in acids and combines with them like a base, forming salts, which are easily decomposed, even by water. From its solution in strong hydrochloric acid, water throws down orange-yellow laminæ, free from hydrochloric acid after slight washing; the crystals obtained from a solution in nitric acid are also free from acid when thoroughly washed (Strecker).

*Sulphate of Cacotheline.* — A solution of cacotheline in sulphuric acid deposits yellow crystals, which retain sulphuric acid after washing with alcohol (Strecker).

*Chloroplatinate of Cacotheline.* — From a solution of cacotheline in

strong hydrochloric acid, bichloride of platinum throws down, after long standing, yellow needles, to which the solution afterwards solidifies. The crystals are washed with water and ether-alcohol. — Lemon-yellow: stable at 100°; explodes when cautiously heated (Strecker).

| | | | | | | Strecker. |
|---|---|---|---|---|---|---|
| $C^{40}N^2X^2H^{22}O^{10}$,HCl,2Cl | .... | 569·5 | ... .... | 85·18 | | |
| Pt | ................................. | 98·7 | ........ | 14·82 | ........ | 14·4—14·8 |
| $C^{40}N^2X^2H^{22}O^{10}$,HCl,PtCl². | .... | 668·2 | ........ | 100·00 | | |

*C. With Oxides.* — Cacotheline dissolves easily in aqueous ammonia, potash, or baryta; the ammoniacal solution throws down a flocculent precipitate from neutral acetate of lead and silver-salts (Strecker). — The solution in *ammonia-water* turns green, and ultimately brown, when warmed (Laurent; Strecker). After the free ammonia, alcohol throws down from the solution, blackish-green flocks, the green aqueous solution of which is precipitated green by acetic acid and by neutral acetate of lead or nitric acid (Gerhardt). On one occasion the ammoniacal solution deposited a base containing hyponitric acid, insoluble in water and alcohol, but easily soluble in hydrochloric acid, and precipitated from the solution by ammonia as a yellow jelly, and by bichloride of platinum as a reddish-yellow double salt. This double salt, when dried, turns black, with a golden-green reflex, but when moistened with a drop of alcohol, it again becomes reddish-yellow; when very highly dried, it appears of a bluish-red colour, which is changed to orange-red by a drop of water. It dissolves in oil of vitriol with fine rose-red colour, changing to lilac when strongly heated. It explodes when heated alone, leaving 23 p. c. of platinum (Laurent).

The solution of cacotheline in caustic potash is brownish-yellow (Gerhardt).

*Cacotheline-Baryta.* — When cacotheline is boiled with water and carbonate of baryta, carbonic acid is evolved, and a deep-brown solution formed, from which an amorphous brown powder is deposited on standing, and more on the addition of alcohol. The powder is soluble in water with brown colour. — After drying in a vacuum, it loses 10·5 p. c. of water at 120° (7 at. = 10·5 p. c. HO) (Strecker).

| | | *Dried.* | | | Strecker. |
|---|---|---|---|---|---|
| $C^{40}N^2X^2H^{22}O^{10}$ | ............ | 462 | ........ | 85·78 | |
| BaO | ............................ | 76·5 | ........ | 14·22 | ........ 14·1 |
| $C^{40}N^2X^2H^{22}O^{10}$,BaO. | .... | 538·5 | ........ | 100·00 | |

*Cacotheline with Lead-oxide.* — From a solution of neutral acetate of lead, mixed with nitrate of cacotheline, ammonia throws down yellow flocks, which, after drying at 100°, contain 57·6 p. c. lead-oxide, or about 6 at. to 1 at. of cacotheline (Strecker).

*Cacotheline with Silver-oxide.* —Obtained in the same way as the lead-compound, nitrate of silver being substituted for acetate of lead. Yellow precipitate, containing 21·6 p. c. of silver, or 1 at. to 1 at. of cacotheline (Strecker).

Cacotheline dissolves slightly in alcohol, according to Laurent. It is easily soluble in boiling alcohol and *ether*, before drying, but nearly insoluble after drying (Gerhardt).

*Primary Nucleus* $C^{40}H^{36}$; *Oxygen-nucleus* $C^{40}H^{34}O^2$.

## Ursone.

$$C^{40}H^{34}O^4 = C^{40}H^{34}O^2,O^2.$$
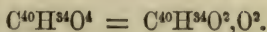
H. TROMMSDORFF. *N. Br. Arch.* 80, 273; *Chem. Centr.* 1855, 115.
HLASIWETZ. *Wien. Acad. Ber.* 16, 293; *N. Br. Arch.* 85, 15; *J. pr. Chem.* 66, 123.

*Source.*—In the leaves of *Arbutus Uva Ursi* (Trommsdorff).

*Preparation.* The coarsely-powdered leaves are exhausted with ether, and the crystalline deposit which forms in the extract is washed with ether and crystallised from alcohol. — In the preparation of arbutin (xv, 419) ursone remains in that portion of the alcoholic extract which is insoluble in water, and may be obtained by washing with ether and boiling with alcohol. In the latter case it is to be purified by washing with ether and recrystallising from alcohol, with the help of animal charcoal (Trommsdorff).

*Properties.* Colourless, silky needles (Trommsdorff), which melt at 198°—200°, and solidify to a crystalline mass, or when heated above their melting-point, to an amorphous, fissured mass (Hlasiwetz). Boils at a higher temperature, and sublimes apparently unaltered (Trommsdorff).

|  | *at 100°.* |  |  |  | Hlasiwetz. *mean.* |
|---|---|---|---|---|---|
| 40 C | 240 | .......... | 78·43 | .......... | 78·40 |
| 34 H | 34 | .......... | 11·11 | .......... | 11·17 |
| 4 O | 32 | .......... | 10·46 | .......... | 10·43 |
| $C^{40}H^{34}O^4$ | 306 | .......... | 100·00 | .......... | 100·00 |

According to Hlasiwetz, it has the formula $C^{20}H^{17}O^2$ and is allied to hartin.

Ursone burns with a yellow smoky flame, without leaving charcoal. It dissolves partially, with orange colour in cold *oil of vitriol*, and carbonises when heated therewith, evolving sulphurous acid. — With *fuming nitric acid* it evolves a little nitric oxide, and forms a yellow solution, precipitable by water (Trommsdorff).

Ursone is insoluble in *water* and in *dilute acids* and *alkalis*, and but slightly soluble in *alcohol* and *ether* (Trommsdorff).

*Oxygen-nucleus* $C^{40}H^{30}O^6$.

## Arnicin.

? $C^{40}H^{30}O^8 = C^{40}H^{30}O^6,O^2.$
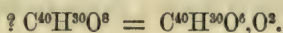
LEBOURDAIS. *N. Ann. Chim. Phys.* 24, 63; *Ann. Pharm.* 67, 251; *J. pr. Chem.* 45, 363.

WALZ.  *N. Jahrb. Pharm.* 13, 175 ; 14, 79 ; *Pharm. Viertelj.* 10, 188 ;
  *Kopp's Jahresber.* 1860, 544. — *N. Jahrb. Pharm.* 15, 329 ; *N. Br.
  Arch.* 108, 1 ; *Pharm. Viertelj.* 11, 1 ; *Kopp's Jahresber.* 1861, 752.

The bitter principle of *Arnica montana* (Handbuch, viii. [2], 66).  From this
plant, Pfaff (*Syst. der Mat. med.* 3, 209), and Chevallier & Lassaigne (*Taschenbuch*,
1821, 91) obtained resins, Bastick an amorphous alkaloïd, Pavesi a resin allied to
santonin.  Peretti, by distilling arnica-flowers with solution of caustic potash,
obtained a volatile base, which O. Hesse (*Ann. Pharm.* 129, 254) recognised as
ammonia with traces of trimethylamine. — Arnicin occurs more abundantly in the
flowers than in the root (Walz).

*Preparation.*  A. *From the root.*  Arnica-root is freed from volatile
oil by distillation with water ; the residue is pressed and exhausted
with alcohol ; the tincture is digested with oxide of lead ; and the dis-
solved lead is removed by means of hydrosulphuric acid.  The alcohol
is then distilled off, and the residue evaporated to dryness, after which
the arnicin is extracted by ether.  The ethereal solution is shaken
with solution of caustic potash, to which it gives up fat and colouring
matter, and after separation from the alkaline liquid, it is treated with
animal charcoal and evaporated to dryness.  The residue is dissolved
in weak alcohol, and the filtrate evaporated or precipitated with water.
In this way 13 pounds of the root yield about an ounce of arnicin
(Walz).

B. *From Arnica flowers.*  1. The flowers are exhausted with ether ;
the ether is distilled off ; and the arnicin is extracted from the residual
fatty mass by alcohol of sp. gr. 0·85.  A little fat which is taken up
at the same time may be separated by repeated solution in weak
alcohol.  Purification is effected by animal charcoal. — 2. The alcoholic
tincture of the flowers is treated with animal charcoal to remove
chlorophyll ; the filtrate is evaporated, and the residue exhausted with
ether ; the fat and arnicin taken up thereby are separated as in 1. —
3. An aqueous decoction of the flowers is precipitated by tannic
acid, and the precipitate is washed (not too long), dried, triturated,
and exhausted with alcohol.  The solution is agitated with levigated
oxide of lead to remove tannic acid, filtered, treated with hydrosul-
phuric acid, and freed from alcohol by distillation, whereupon fat is
deposited, to remove which the arnicin is precipitated by water.  The
precipitate is purified by washing it with water, dissolving in alcohol,
digesting the solution with animal charcoal, and precipitating with
water.  It is then dissolved in ether and left to evaporate (Walz).

Lebourdais allows a strong aqueous infusion of the flowers to run
slowly through a thick layer of purified animal charcoal, which takes
up colouring matter and the bitter principle.  He then washes the
charcoal with water, dries, and exhausts it with hot alcohol.  On
evaporating the filtrate, the arnicin remains as a neutral turpentine-
like mass, very slightly soluble in water, but soluble in all proportions
in alcohol. — On attempting to precipitate the colouring matter with
neutral acetate of lead, before treating with animal charcoal, the
greater part of the arnicin is thrown down at the same time (Lebour-
dais).

Bastick's alkaline *arnicin* is extracted from the flowers by alcohol
containing sulphuric acid.  The tincture is digested with a slight
excess of lime and filtered ; the filtrate is saturated with dilute sul-

phuric acid, again filtered, and evaporated; the resin thereby thrown down is removed, and the liquid is exactly neutralised with carbonate of potash and separated from the resulting precipitate. The filtrate is then shaken with a large excess of carbonate of potash and ether, to which it gives up the arnicin. Thus obtained, arnicin is bitter, alkaline, soluble in water, alcohol, and ether, and combines with acids to form crystallisable salts, which are precipitated in dense flocks by tincture of galls (Bastick, *Pharm. Journ.* 3, 386; *Jahrb. pr. Pharm.* 24, 44; *N. J. Pharm.* 19, 454).

Pavesi (*J. Médic. de Bruxelles*, 1859, 61; abstr. *Pharm. Viertelj.* 9, 290) prepares arnicin in the same manner as santonin (xvi, 249) by extraction with lime and alcohol. He thus obtains a dark-yellow, viscid, nauseously bitter resin, insoluble in water, but soluble in alkalis, and precipitable therefrom by acids. It dissolves slightly in alcohol and ether.

*Properties.* — Walz's arnicin forms a golden-yellow, amorphous mass, free from nitrogen.

|  |  |  |  |  | Walz. mean. | at 100°. |
|---|---|---|---|---|---|---|
| 40 C | 240 | .......... | 71·85 | .......... | 71·78 |
| 30 H | 30 | .......... | 8·99 | .......... | 9·19 |
| 8 O | 64 | .......... | 19·16 | .......... | 19·03 |
| $C^{40}H^{30}O^8$ | 334 | .......... | 100·00 | .......... | 100·00 |

Walz's earlier formula, $C^{70}H^{54}O^{14}$, agrees very nearly with these numbers.

Arnicin is decomposed by boiling with *acids*, with separation of dark flocks. It is, however, not a glucoside. — It hardens with *nitric acid*, and assumes a yellowish-brown colour with oil of vitriol, without undergoing solution. — When alcoholic arnicin is heated for some time to 100° with *caustic potash*, and the residue is distilled with dilute sulphuric acid, a large quantity of resinous flocks is deposited, whilst oil and acid water, containing valerianic or butyric acid, pass over (Walz).

Arnicin dissolves only slightly in *water*, but is soluble in aqueous *ammonia* and in *alkalis*. Its alcoholic solution forms crystals with *caustic baryta*. It forms a white precipitate with basic acetate of lead, also with solutions of silver-oxide, mercurous oxide, and platinic oxide. — Arnicin is soluble in *ether* (Walz).

*Resins of Arnica-root.* — A. *Resin soluble in ether.* When an alcoholic tincture of the root, previously exhausted with water, is freed from substances precipitable by oxide of lead and from oxide of lead taken up at the same time, then evaporated and exhausted with ether, this liquid takes up the arnicin. The portion remaining undissolved, when mixed with an acid, yields flocks of the resin, which is purified by dissolving in alcohol, digesting with animal charcoal, and precipitating with water. — It forms a clear, yellowish-brown mass, which is soft and pasty at 100°. Has a peculiar odour, and a somewhat acrid taste. Contains 65·72 p. c. C., 8·50 H., and 25·78 O., corresponding to the formula $C^{40}H^{30}O^{12}$ (65·57 C., 8·19 H.) (Walz).

B. *Resin insoluble in ether.* — When the portion of the alcoholic extract insoluble in ether is treated with water, the yellow colouring

matter is dissolved, whilst this resin remains behind. It is purified by dissolving it in alcohol and precipitating with water. — Dark-brown, easily pulverisable mass, having a harsh taste. Contains 51·81 p. c. C., 6·5 H., and 41·69 O., corresponding to the formula $C^{40}H^{30}O^{24}$ (51·5 C., 6·45 H.) (Walz).

*Arnica yellow.* — Amorphous yellow mass, soluble in water. The lead-compound contains 30·0 p. c. C., 3·9 H., 21·0 O., and 45·0 PbO. = $C^{44}H^{30}O^{24}$,3PbO. (Walz).

## Oxygen-nucleus $C^{40}H^{28}O^8$.

## Elaterin.

$$C^{40}H^{28}O^{10} = C^{40}H^{28}O^8,O^2.$$
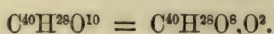
HENNEL.    *J. Royal Inst.* 1, 532.
MORRIES.    *Edin. Med. and Surg. Journ.* No. 107, 339 ;   *Repert.* 39, 134.
CL. MARQUART.    *Repert.* 46, 8.
GOLDING BIRD.    *Repert.* 73, 222.
ZWENGER.    *Ann. Pharm,* 43, 359.
WALZ.    *N. Jahrb. Pharm.* 11, 21, and 178.

Braconnot (*J. Phys.* 84, 294) described a bitter substance, Paris (*Répert.* 13, 270) a soft resin, from ecbalium, as *Elaterin.*

*Source.* In the fruit of *Ecbalium Elaterium* (*Handbuch*, viii, 37) and in the powder which is deposited from the sap, the officinal *Elaterium album* and *nigrum.* — The fruit collected in autumn contains no elaterin, but only chlorophyll (Marquart), or at least the elaterin is less easily prepared from it, and is obtained only in small quantity (Walz). *Elaterium album* contains 15 to 26 p. c. (Morries), 40 p. c. (Hennel), 50 p. c. (Walz) of elaterin.

*Preparation.* 1. White elaterium is exhausted with boiling alcohol; the tincture is evaporated to half its bulk, and the elaterin is precipitated by boiling water. It still requires to be purified by washing with ether and crystallising from absolute alcohol (Zwenger). — 2. The portion of elaterium insoluble in water is exhausted with alcohol, and the tincture is evaporated to an oil, and poured while still warm into boiling caustic potash. The chlorophyll is thereby retained in solution, whilst the elaterin is gradually thrown down as a crystalline precipitate, which is purified by washing with water (Morries).

3. The expressed juice of the fruit is evaporated to an extract, which is exhausted with alcohol; the solution is precipitated with alcoholic neutral acetate of lead; the filtrate is freed from lead by hydrosulphuric acid, and evaporated; the residue is exhausted with ether; the undissolved portion taken up by alcohol; and the elaterin precipitated from the alcoholic solution by water. The ether dissolves a little elaterin, which remains behind on evaporating the ethereal extract and exhausting the residue, first with water and then

with ether. — The pressed fruit still contains elaterin, which may be obtained by extraction with alcohol (Walz).

*Properties.* Colourless, shining, six-sided tables (Zwenger); rhombic needles striated on the sides (Morries). Melts [between 100° and 150° (Hennel); a little over 100° (Morries)] exactly at 200°, first becoming yellow, to a transparent yellowish amorphous mass, which cracks on cooling (Zwenger). — Tastes very bitter (Hennel), bitter and styptic (Morries), very slightly acrid alone, and extremely bitter when dissolved in alcohol (Marquart). — $\frac{1}{4}$th of a grain kills a dog in a day or two (Morries). Its acts as an extremely powerful cathartic and emetic (Marquart). — Neutral. Free from nitrogen (Zwenger).

|  | at 100°. |  |  |  | Zwenger. mean. |
|---|---|---|---|---|---|
| 40 C ................ | 240 | ............ | 68·96 | ............ | 68·46 |
| 28 H ................ | 28 | ............ | 8·04 | ............ | 8·22 |
| 10 O ................ | 80 | ............ | 23·00 | ............ | 23·32 |
| $C^{40}H^{28}O^{10}$ ........ | 348 | ............ | 100·00 | ............ | 100·00 |

According to Zwenger the formula is $C^{20}H^{14}O^5$.

*Decompositions.* Elaterin decomposes when strongly *heated*, evolving white fumes having a somewhat suffocating odour, and burns with a smoky flame (Zwenger). — It dissolves in *oil of vitriol* with dark-red colour, and is precipitated from the solution as a brown substance by water (Zwenger; Morries). The solution is rendered pale red by permanganate of potash (Guy). — Elaterin is decomposed by *nitric acid*, forming a transparent gum (Morries). See below.

Elaterin is insoluble in *water*. — It dissolves in fuming *nitric acid*, from which it is precipitated unaltered by water (Zwenger). — It is insoluble in dilute *acids* and *alkalis*, and does not precipitate alcoholic solutions of metallic salts. Aqueous solutions of metallic salts precipitate elaterin from its alcoholic solution in the same manner as water (Zwenger).

Elaterin dissolves in 15 parts of cold, and 2 parts of hot *alcohol*, and in 290 parts of *ether* (Hennel). It is slightly soluble in cold, and easily soluble in hot *oil of turpentine* (Marquart), and in hot *olive oil* (Morries).

*Appendix to Elaterin.*

# 1. Prophetin.

## ? $C^{46}H^{36}O^{14}$.
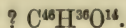
Walz & Winckler. *N. Jahrb. Pharm.* 11, 31.
Walz. *N. Jahrb. Pharm.* 11, 178.

*Source.* In *Cucumis Prophetarum* and in *Ecbalium Elaterium*.

*Preparation.* A. *From the fruit of Cucumis Prophetarum.* — The juice of the fruit, clarified by standing and boiling, is evaporated over

the water-bath to a syrup, and, after cooling, mixed with 4 times its volume of 80 p. c. alcohol and filtered. The alcohol is separated by distillation, and the residue, evaporated to a thin syrup, is shaken with ether so long as it gives up a bitter substance. The ethereal solution leaves, on evaporation, a turpentine-like residue, which dries up over the water-bath to a white, resinous, friable mass (Winckler).

B. *From Ecbalium Elaterium.* — Together with ecbalin, hydro-elaterin, and elateride. — The entire plant, dried and coarsely powdered, is exhausted with boiling alcohol; the extract is mixed with water, and the alcohol distilled off; and the aqueous liquid, filtered from the resin which is deposited, is employed for the preparation of prophetin, hydro-elaterin, and elateride. The resin is used for the preparation of ecbalin.

a. *Preparation of Prophetin.* — The solution is precipitated with neutral acetate of lead, filtered, and again precipitated with basic acetate of lead; this second precipitate is likewise removed or is redissolved in a large quantity of water [the precipitate contains prophetin and elateride : it is doubtful to me which process Walz intends to indicate (Kr.)]; the dissolved lead is removed by the addition, first of an insufficient quantity of sulphuric acid and then of carbonate of soda; the slightly alkaline solution is precipitated by aqueous tannic acid (an excess of which redissolves the precipitate); the precipitate is washed slightly, pressed, and digested in alcohol; and the filtered alcoholic solution is shaken up with hydrated oxide of lead, filtered, and concentrated, whereupon the prophetin is slowly deposited in the form of a white powder. This and the quantity subsequently obtained is washed with water, dissolved in alcohol, and crystallised by adding water till cloudiness is produced, and leaving it at rest.

b. *Preparation of Hydro-elaterin and Elateride.* — The mother-liquor from which prophetin has been separated is evaporated to dryness; the residue is redissolved in water and evaporated; and the hydro-elaterin is extracted from the residue by ether, whilst elateride remains undissolved. The latter body is purified by dissolving it in absolute alcohol, and evaporating the filtered solution.

c. *Preparation of Ecbalin.* — The resin obtained as above is dissolved in ether; the solution is digested with animal charcoal and filtered; the ether is distilled off; and the residue, after drying completely at 100°, is again dissolved in ether, and digested with animal charcoal. The filtered solution is then evaporated, or precipitated with water.

*Properties.* Prophetin forms a yellowish-white powder, seen under the microscope to consist of resinous granules. It loses 2·5 p. c. in weight over the water-bath. Free from nitrogen. Tastes very bitter.

| | Dried ? | | | | | Walz. a. | | | Walz. b. mean. |
|---|---|---|---|---|---|---|---|---|---|
| 46 C | 276 | ........ | 65·09 | ........ | 64·91 | to | 65·75 | ........ | 64·80 |
| 36 H | 36 | ........ | 8·49 | ........ | 8·39 | ,, | 8·48 | ........ | 7·57 |
| 14 O | 112 | ........ | 26·42 | ........ | 26·70 | ,, | 25·77 | ........ | 27·63 |
| $C^{46}H^{36}O^{14}$ | 424 | ........ | 100·00 | ........ | 100·00 | ,, | 100·00 | ........ | 100·00 |

Walz calculates his analyses incorrectly (Kr.). — *a* was obtained from Cucumis, *b* from Ecbalium.

*Decompositions.* Prophetin dissolves in *oil of vitriol* with red-brown colour. — When boiled with *hydrochloric acid*, it breaks up into sugar and *propheretin*, which separates in the form of a resin, and after washing and dissolving in ether, remains as an amorphous resin (Walz subsequently obtained crystals), containing, on the average (from Cucumis), 71·11 p. c. C., 9·12 H., and 19·77 O. From these numbers Walz calculates the formula $C^{40}H^{30}O^8$ (71·85 p. c. C., 9·00 H.), and represents the decomposition by the equation—

$$C^{46}H^{36}O^{14} = C^{40}H^{30}O^8 + \tfrac{1}{2}C^{12}H^{12}O^{12}.$$
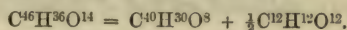
On one occasion he obtained from prophetin 78·5 p. c. of propheretin and 19·5 p. c. of sugar, on another occasion 34 p. c. of sugar.

*Combinations.* Prophetin dissolves slightly in cold, and in 200 parts of boiling *water*. It dissolves in *alcohol* of 80 p. c., and in nearly all proportions of absolute alcohol, from which it is precipitated by water. It is freely soluble in *ether*. It is precipitated by aqueous *tannic acid* in white flocks.

## 2. Ecbalin *or* Elateric acid. — Preparation see above. Yellow, soft resin. Very bitter and acrid. It is converted by chlorine-water into a white friable substance, and is decomposed by nitric acid, with deep red coloration, and also by oil of vitriol. — It dissolves in 20 parts of water, and is soluble in aqueous alkalis, from which it is precipitated by acids, and in alcohol and ether.

Lead-salts precipitate ecbalin (Walz).

| | | | | Calculation according to *Walz*. | | Walz. mean. |
|---|---|---|---|---|---|---|
| 40 C | 240 | | 71·01 | | | 71·44 |
| 34 H | 34 | | 10·06 | | | 10·48 |
| 8 O | 64 | | 18·93 | | | 18·08 |
| $C^{40}H^{34}O^8$ | 338 | | 100·00 | | | 100·00 |

## 3. Hydroelaterin. — Yellow, amorphous, friable mass, soluble in water, alcohol, and ether. Does not yield sugar with acids. The solution in caustic potash is precipitated by acids.

| | | | Calculation according to *Walz*. | | Walz. | |
|---|---|---|---|---|---|---|
| 40 C | 240 | | 65·57 | | 64·81 | 65·38 |
| 30 H | 30 | | 8·19 | | 8·01 | 8·06 |
| 12 O | 96 | | 26·24 | | 27·18 | 26·56 |
| $C^{40}H^{30}O^{12}$ | 366 | | 100·00 | | 100·00 | 100·00 |

## 4. Elateride. — Intensely bitter substance, precipitated, unaltered from its solution in strong acids by water, without forming sugar. Insoluble in water and ether, but soluble in alcohol and alkalis, from the latter of which it is precipitated by acids.

| | | | Calculation according to *Walz*. | | Walz. at 100°. | |
|---|---|---|---|---|---|---|
| 40 C | 240 | | 51·72 | | 52·66 | 52·09 |
| 32 H | 32 | | 6·89 | | 6·89 | 6·76 |
| 24 O | 192 | | 41·39 | | 40·45 | 41·15 |
| $C^{40}H^{32}O^{24}$ | 264 | | 100·00 | | 100·00 | 100·00 |

Walz calculates all these analyses incorrectly (Kr.).

*Oxygen-nucleus* $C^{40}H^{24}O^{12}$.

## Coriamyrtin.

$$C^{40}H^{24}O^{14} = C^{40}H^{24}O^{12},O^2.$$
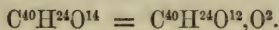
RIBAN.  *Par. Soc. Bull.* 6, 87; *N. J. Pharm.* 45, 487; abstr. *Compt. rend.* 57, 798; *Chem. Centr.* 1864, 367; *Pharm. Viertelj.* 14, 93.

A glucoside contained in the leaves and fruit of *Coriaria myrtifolia*.

*Preparation.* The sap of the fresh plant, or the aqueous decoction of the dried plant, is precipitated by basic acetate of lead, and filtered; and the liquid, freed from excess of lead by hydrosulphuric acid, is evaporated to a syrup. When shaken with ether, the syrup gives up to that liquid the coriamyrtin, which remains on evaporation, and is purified by crystallisation from alcohol. 100 pounds of the young shoots yield 7·5 grammes of impure crystals.

White, inodorous four- or six-sided prisms, apparently monoclinic. Very bitter and poisonous. Exerts a right-handed action on polarised light. Does not lose weight at 200°; melts at 220° to a colourless liquid, which solidifies in a crystalline mass. Neutral. Free from nitrogen.

|  | *at 109°.* |  |  |  | Riban. |  |  |
|---|---|---|---|---|---|---|---|
| 40 C ............... | 240 | ........ | 63·86 | ........ | 63·69 | ........ | 63·90 |
| 24 H ............... | 24 | ........ | 6·38 | ........ | 6·56 | ........ | 6·49 |
| 14 O ............... | 112 | ........ | 29·76 | ........ | 29·75 | ........ | 29·61 |
| $C^{40}H^{24}O^{14}$ ........ | 376 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Coriamyrtin turns brown on prolonged *fusion*, and afterwards carbonises. — It is rapidly decomposed by warming with *nitric acid*, forming a clear solution. Other *acids*, including acetic and oxalic, decompose it, with formation of sugar and resin. *Emulsin* does not act upon it.

Coriamyrtin dissolves in 70 parts of water at 22°, and slightly in boiling water. The solution is not precipitated by chloride of platinum or phosphomolybdic acid.

Nearly insoluble in *bisulphide of carbon*. Dissolves in 49·7 parts of 86 p. c. alcohol at 22°, and very freely in boiling *alcohol*, crystallising on cooling. Dissolves in *ether, chloroform,* and *benzene*.

*Primary Nucleus* $C^{40}H^{38}$; *Oxygen-nucleus* $C^{40}H^{34}O^4$.

## Asclepione.

$$C^{40}H^{34}O^6 = C^{40}H^{34}O^4,O^2.$$
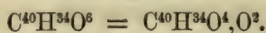
C. LIST.  *Ann. Pharm.* 69, 125; abstr. *Pharm. Centr.* 1849, 283.

Discovered by List in the milk-sap of *Asclepias syriaca* (Handbuch viii, [2], 57), John (*Chem. Schr.* 2, 26) having previously described a resin obtainable therefrom.

A resinous substance and a bitter principle (*Asclepiadin, Asclepin*)

from *Asclepias Vincetoxicum* have been described by Feneulle (*J. Pharm.* 11, 305).

The sap which flows from incisions in *Asclepias syriaca* curdles when warmed, from coagulation of albumin, which encloses the asclepione. The coagulum is exhausted with ether to remove the asclepione, which, after evaporating the ether, crystallises on further concentration of the remaining clear liquid. The product is purified by dissolving it in anhydrous ether, a foreign substance then remaining undissolved.

White, cauliflower-like mass, forming when slowly evaporated, delicate radiated tufts. Inodorous and tasteless. Melts at 104°, and solidifies on cooling to an amorphous, transparent mass.

|  |  |  |  |  | List. mean. |
|---|---|---|---|---|---|
| 40 C | 240 | ............ | 74·54 | ............ | 74·68 |
| 34 H | 34 | ............ | 10·56 | ............ | 10·61 |
| 6 O | 48 | ............ | 14·90 | ............ | 14·71 |
| $C^{40}H^{34}O^6$ | 322 | ............ | 100·00 | ............ | 100·00 |

*Asclepione*, when *heated* above its melting-point, assumes a yellow colour, and evolves an odour of caoutchouc. — It dissolves unaltered in hot strong *caustic potash*.

Insoluble in *water* and *alcohol*, but easily soluble in *ether*, and less freely in *acetic acid*, *rock-oil*, and *oil of turpentine*.

*Oxygen-nucleus* $C^{40}H^{24}O^{14}$.

# Xanthoxylin.

$$C^{40}H^{24}O^{16} = C^{40}H^{24}O^{14},O^2.$$
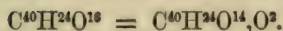
STENHOUSE. *N. Phil. Mag.* 7, 28; *Ann. Pharm.* 89, 251; *J. pr. Chem.* 61, 497; *Kopp's Jahresber.* 1854, 639. — *Ann. Pharm.* 104, 326; *Pharm. Journ.* 17, 19; *J. pr. Chem.* 73, 179; *Kopp's Jahresber.* 1857, 482.

Occurs in Japan pepper, the fruit of *Xanthoxylum piperatum* or *alatum* (Handbuch, viii [2], 21). — On distilling the ground pepper with water, a floating oil is obtained, from which the xanthoxylin separates on cooling; it remains behind when the oil is freed from xanthoxylene (xiv, 315) by distillation at 130°. — Xanthoxylin crystallises also on concentrating the alcoholic tincture, and may be freed from resin by washing it with cold aqueous ammonia. It is purified by recrystallisation from ether or alcohol.

Large, colourless crystals of the oblique prismatic system, having a silky lustre. Fig. 85 without *f*. Angle $i : t = 90°$; $\alpha : t = 142°50'$; $\alpha : i = 127° 10'$; $u : t = 121° 10'$; $u$ in front: $i = 96° 30'$. The crystals are tabular in form from predominance of $i$; $\alpha$ and $u$ imperfectly formed. Cleavable parallel to $t$ and $i$ (Miller). — Xanthoxylin is susceptible of distillation. It melts at 80° and solidifies at 78°. Has a faint odour like stearin and an aromatic taste. Neutral.

| | | | | | | | | Stenhouse. |
|---|---|---|---|---|---|---|---|---|
| 40 C | 240 | ........ | 61·22 | ........ | 61·09 | ........ | 60·97 |
| 24 H | 24 | ........ | 6·12 | ........ | 6·62 | ........ | 6·14 |
| 16 O | 128 | ........ | 32·66 | ........ | 32·29 | ........ | 32·89 |
| $C^{40}H^{24}O^{16}$ | 392 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Xanthoxylin is converted by *nitric acid* into oxalic acid. It is insoluble in water, but easily soluble in *alcohol* and *ether*. The alcoholic solution is not precipitated by alcoholic neutral acetate of lead or nitrate of silver, even with addition of ammonia (Stenhouse).

*Primary Nucleus* $C^{40}H^{40}$.

## Arachidic Acid.

$$C^{40}H^{40}O^4 = C^{40}H^{40},O^4.$$
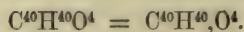
HEINTZ. *Pogg.* 90, 146.
GÖSSMANN. *Ann. Pharm.* 89, 1; *J. pr. Chem.* 61, 336.
SCHEVEN & GÖSSMANN. *Ann. Pharm.* 97, 257; *J. pr. Chem.* 68, 179.
CALDWELL. *Ann. Pharm.* 101, 97; *J. pr. Chem.* 71, 192.

*Butic acid.* — Discovered by Heintz in butter, and afterwards by Gossman in earth-nut oil.

*Preparation. From Earth-nut oil.* — The solid fatty acids obtained by saponifying the oil and decomposing the soap, are macerated with five or six times their volume of alcohol. The liquid is filtered, and the residue is pressed, and afterwards dissolved in 20 times its weight of boiling alcohol, whereupon, on cooling, impure arachidic acid separates in laminæ, which are purified by repeated recrystallisation from absolute alcohol till they melt at 75°, and freed from adhering green resin by solution in warm ether (Gössmann).

A further portion of the acid may be obtained by partial precipitation of the alcoholic mother-liquors with acetate of magnesia (somewhat in the manner described at p. 355, vol. xvi), the arachidic acid going down with the first portions of the precipitate (Gössmann).

On submitting the solid fatty acids of butter to fractional precipitation, the arachidic acid is thrown down in the first portions of the precipitate, but cannot be completely separated from stearic acid, even when four pounds of butter are employed (Heintz). See xvi, 210, 354.

*Properties.* Very small, shining laminæ, having a pearly lustre after pressing. Melts at 75°, and solidifies in a radiated mass at 73·5°. When kept it turns white and porcelain-like.

| | | | | | Gössmann. mean. | | Heintz. mean. |
|---|---|---|---|---|---|---|---|
| 40 C | 240 | ........ | 76·92 | ........ | 76·84 | ........ | 76·55 |
| 40 H | 40 | ........ | 12·82 | ........ | 12·86 | ........ | 12·80 |
| 4 O | 32 | ........ | 10·26 | ........ | 10·30 | ........ | 10·65 |
| $C^{40}H^{40}O^4$ | 312 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Heintz's acid melting at 60·75° still contained stearic acid.

Arachidic acids forms with *glycerin*, mono-, di-, and triarachin (see ix, 490; xvi, 358; and xvii, 373). Scheven & Gössmann described as *arachin* a product melting at 70°, and containing, on the average, 76·21 p.c. C., and 12·57 H., obtained by heating arachidic acid to 210° with excess of glycerin : according to them, the body is represented by the formula $C^{126}H^{124}O^{14} (= 3C^{40}H^{40}O^4 + C^6H^8O^6 - 4HO)$. According to Berthelot, this product is a mixture of diarachin and free arachidic acid.

The *salts* of arachidic acid resemble the stearates and palmitates. They are, for the most part, difficultly soluble.

*Arachidate of Ammonia.* A warm alcoholic solution of the acid, mixed with excess of ammonia, deposits the salt on cooling, in needles, which, after drying, crumble to a loose white powder and give up ammonia.

*Arachidate of Potash.* — *Mono-acid.* — Arachidic acid is boiled with a strong solution of caustic potash for several days, or until combination is complete ; the solution is evaporated to dryness ; and the residue is exposed for some time to air containing carbonic acid, and afterwards exhausted with alcohol. — The salt is deposited from a strong alcoholic solution in the form of a jelly, which falls to a loose crystalline powder on the filter, and from a more dilute solution in distinct crystals. — With 15 or 20 times its weight of boiling water, it forms a clear solution which, when largely diluted, deposits shining laminæ of a bi-acid salt.

| | | | | Scheven & Gössmann. |
|---|---|---|---|---|
| $C^{40}H^{39}O^3$ | 303 | ........ | 86·52 | ----- |
| KO | 47·2 | ........ | 13·48 | ........ 13·01 |
| $C^{40}H^{39}KO^4$ | 350·2 | ........ | 100·00 | |

*Arachidate of Baryta.* — White, light, crystalline powder, insoluble in water, but soluble in a large quantity of boiling alcohol.

| | | | | Scheven & Gössmann. | | | Heintz. |
|---|---|---|---|---|---|---|---|
| $C^{40}H^{39}O^3$ | 303 | ........ | 79·85 | ........ | | ........ | 79·73 |
| BaO | 76·5 | ........ | 20·15 | ........ | 19·72 | ........ | 20·27 |
| $C^{40}H^{39}BaO^4$ | 879·5 | ........ | 100·00 | ........ | | ........ | 100·00 |

*Arachidate of Strontia.* — Dissolves more easily than the baryta-salt in boiling alcohol, from which it is deposited in the form of a crystalline powder on cooling.

| | | | | Scheven & Gössmann. |
|---|---|---|---|---|
| $C^{40}H^{39}O^3$ | 303 | ............ | 85·36 | |
| SrO | 52 | ............ | 14·64 | ............ 14·0 |
| $C^{40}H^{39}SrO^4$ | 355 | ............ | 100·00 | |

*Arachidate of Lime* is a loose, lustrous powder.

*Arachidate of Magnesia.* — On mixing alcoholic arachidate of ammonia with an alcoholic solution of acetate of magnesia, this salt is deposited as an amorphous precipitate, which dissolves on boiling and crystallises from the solution as it cools. — White, loose, crystalline powder, insoluble in water but slightly soluble in alcohol.

| | | | | | | |
|---|---|---|---|---|---|---|
| $C^{40}H^{39}O^3$ ............... | 303 | ........ | 93·81 | | |
| MgO ................... | 20 | ........ | 6·19 | ........ | 6·27 |

| | | | |
|---|---|---|---|
| $C^{40}H^{39}MgO^4$ ........ | 323 | ........ | 100·00 |

*Arachidate of Copper.* Alcoholic acetate of copper throws down from arachidate of ammonia, a blue-green amorphous precipitate, which turns crystalline on standing and crystallises from alcohol in needles. Melts when heated.

Scheven & Gössmann.
*mean.*

| | | | | | |
|---|---|---|---|---|---|
| 40 C ..................... | 240 | ........ | 70·03 | ........ | 70·55 |
| 39 H..................... | 39 | ........ | 11·38 | ........ | 11·58 |
| 3 O ..................... | 24 | ........ | 7·01 | ........ | 6·46 |
| CuO ............ | 40 | ........ | 11·58 | ........ | 11·41 |

| | | | | | |
|---|---|---|---|---|---|
| $C^{40}H^{39}CuO^4$ ........ | 343 | ........ | 100·00 | ........ | 100·00 |

*Arachidate of Silver.* — Obtained by double decomposition as an amorphous precipitate, which crystallises from alcohol in white needles, not altered by exposure to light.

Scheven & Gössmann.

| | | | | | |
|---|---|---|---|---|---|
| $C^{40}H^{39}O^4$ ............ | 311 | ............ | 74·22 | | |
| Ag ..................... | 108 | ............ | 25·78 | ............ | 25·4 |

| | | | |
|---|---|---|---|
| $C^{40}H^{39}AgO^4$ ........ | 419 | ............ | 100·00 |

Arachidic acid is nearly insoluble in cold, but easily soluble in hot *alcohol*. It dissolves very easily in *ether* (Gössmann).

# Arachamide.
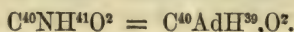
$$C^{40}NH^{41}O^2 = C^{40}AdH^{39},O^2.$$

A mixture of earth-nut oil with excess of strong alcoholic ammonia is allowed to stand for several weeks; the liquid is saturated afresh with ammonia; and when no further change is perceptible, the alcohol and excess of ammonia are removed by warm water. The product is allowed to cool, and the more solid portion is collected, freed from adhering oil by pressing, and repeatedly crystallised from alcohol.

Stellate groups of prisms, melting at 98 to 99°.

Scheven & Gössmann.
*mean.*

| | | | | | |
|---|---|---|---|---|---|
| 40 C ..................... | 240 | ........ | 77·17 | ........ | 77·08 |
| N ..................... | 14 | ........ | 4·50 | ........ | 4·27 |
| 41 H ..................... | 41 | ........ | 13·18 | ........ | 13·11 |
| 2 O ..................... | 16 | ........ | 5·15 | ........ | 5·54 |

| | | | | | |
|---|---|---|---|---|---|
| $C^{40}NH^{41}O^2$ ........ | 311 | ........ | 100·00 | ........ | 100·00 |

Arachamide is insoluble in *water*, but easily soluble in hot *alcohol* of 95 p. c. from which it crystallises on cooling.

## Arachidate of Methyl.

$$C^{42}H^{42}O^4 = C^2H^3O,C^{40}H^{39}O^3.$$
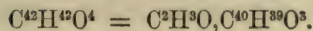
CALDWELL. *Ann. Pharm.* 101, 98.

*Arachinsaures Methyloxyd.*

Formed by passing hydrochloric acid gas into a solution of arachidic acid in wood-spirit, and purified by crystallisation from alcohol.

White, pearly scales. Melts at 54 to 54·5°, and solidifies to a semi-transparent, crystalline mass. — Not volatile without decomposition. Easily soluble in alcohol and ether.

|  |  |  |  |  | Caldwell. |
|---|---|---|---|---|---|
| 42 C | 252 | ........ | 77·30 | ........ | 77·47 |
| 42 H | 42 | ........ | 12·88 | ........ | 12·82 |
| 4 O | 32 | ........ | 9·82 | ........ | 9·71 |
| $C^2H^3O,C^{40}H^{39}O^3$ .... | 326 | ........ | 100·00 | ........ | 100·00 |

## Arachidate of Ethyl.

$$C^{44}H^{44}O^4 = C^4H^5O,C^{40}H^{39}O^3.$$
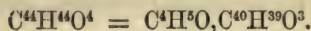
GÖSSMANN. *Ann. Pharm.* 89, 9.
SCHEVEN & GÖSSMANN. *Ann. Pharm.* 97, 261.

*Arachinsaures Aethyloxyd.*

Formed by saturating a solution of arachidic acid in absolute alcohol at 80° or 90° with hydrochloric acid gas, heating for 12 hours, at last to boiling, and precipitating with water. The free arachidic acid is removed by heating the alcoholic solution with aqueous carbonate of soda. The ether is also formed by boiling arachidic acid with alcohol, especially in presence of acetic acid.

Tough, translucent crystalline mass, having a lamellar fracture. Melts at 50°.

|  |  |  |  |  | Gössmann. |
|---|---|---|---|---|---|
| 44 C | 264 | ........ | 77·64 | ........ | 77·60 |
| 44 H | 44 | ........ | 12·94 | ........ | 12·88 |
| 4 O | 32 | ........ | 9·42 | ........ | 9·52 |
| $C^4H^5O,C^{40}H^{39}O^3$ .... | 340 | ........ | 100·00 | ........ | 100·00 |

Arachidate of ethyl is not affected by ammonia gas at 60°, nor by alcoholic ammonia at 100°.

## Monoarachin.

$$C^{46}H^{46}O^8 = C^6H^7O^5,C^{40}H^{39}O^3.$$
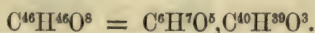
BERTHELOT. *Chim. organ.* 2, 78 ; *N. Ann. Chim. Phys.* 47, 355.

Obtained by heating arachidic acid with glycerin for eight hours to a temperature not exceeding 180°. It is purified with ether and lime (xvi, 359).

Fine granules, melting to a wax. White. Neutral.

Nearly insoluble in cold, and but slightly soluble in boiling ether.

|  |  |  |  |  | Berthelot. |
|---|---|---|---|---|---|
| 46 C | .................... | 276 | ......... | 71·50 | ........ 71·7 |
| 46 H | .................... | 46 | ........ | 11·92 | ........ 12·0 |
| 8 O | .................... | 64 | ........ | 16·58 | ........ 16·3 |
| $C^6H^7O^5,C^{40}H^{39}O^3$ | .... | 386 | ........ | 100·00 | ........ 100·0 |

## Diarachin.

$$C^{86}H^{86}O^{12} \;=\; C^6H^8O^6,2C^{40}H^{39}O^3.$$
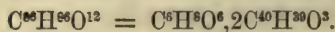
BERTHELOT. *Chim. organ.* 2, 78; *N. Ann. Chim. Phys.* 47, 357.

Concerning Gössmann's *Arachin*, see p. 371.

Formed by heating monoarachin to 200° or 230° for 8 hours with arachidic acid and a trace of water, or by heating arachidic acid to 200° or 230° for 6 hours with glycerin. It is purified by lime and ether (xvi, 359).

Very fine, indistinctly crystalline granules, melting at 75°. White. Neutral.

Almost completely volatile on platinum-foil. — Burns with white flame. — Decomposed completely by lime at 100° in 70 hours.

Nearly insoluble in cold, and very slightly soluble in hot ether; more freely soluble in bisulphide of carbon.

|  |  |  |  | Berthelot. *mean.* |
|---|---|---|---|---|
| 86 C | 516 | ......... | 73·92 | ......... 73·93 |
| 86 H | 86 | ........ | 12·33 | ......... 12·53 |
| 12 O | 96 | ........ | 13·75 | ........ 13·54 |
| $C^6H^8O^6,2C^{40}H^{39}O^3$ .... | 698 | ........ | 100·00 | ......... 100·00 |

## Triarachin.

$$C^{126}H^{122}O^{12} \;=\; C^6H^5O^3,3C^{40}H^{39}O^3.$$
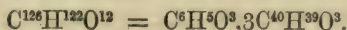
BERTHELOT. *Chim. organ.* 2, 79; *N. Ann. Chim. Phys.* 47, 359.

Obtained by heating a perfectly dry mixture of diarachin within 15 or 20 times its weight of arachidic acid to 200° or 220° for 8 or 10 hours, and purifying the product with lime and ether (xvi, 359).

Neutral mass, very slightly soluble in ether.

|  |  |  |  | Berthelot. |
|---|---|---|---|---|
| 126 C | 756 | ...... | 77·62 | ........ 77·1 |
| 112 H | 122 | ........ | 12·53 | ........ 12·6 |
| 12 O | 96 | ........ | 9·85 | ........ 10·3 |
| $C^6H^5O^3,3C^{40}H^{39}O^3$.... | 964 | ........ | 100·00 | ........ 100·0 |

# Arachidate of Amyl.

$$C^{50}H^{50}O^4 = C^{10}H^{11}O,C^{40}H^{39}O^3.$$
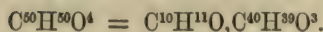
CALDWELL. *Ann. Pharm.* 101, 99.

*Arachinmylester.*

Obtained in the same way as arachidate of methyl, by employing amyl-alcohol instead of wood-spirit.

Shining scales, melting at 44·9° and solidifying at 44° to a semi-transparent crystalline mass. — Decomposes when heated. — Dissolves easily in hot alcohol and ether.

|  |  |  |  |  | Caldwell. |
|---|---|---|---|---|---|
| 50 C | 300 | ........ | 78·53 | ........ | 78·42 |
| 50 H | 50 | ........ | 13·09 | ........ | 13·25 |
| 4 O | 32 | ........ | 8·38 | ........ | 8·33 |
| $C^{10}H^{11}O,C^{40}H^{39}O^3$ | 382 | ........ | 100·00 | ........ | 100·00 |

*Oil of earth-nuts.* From the seeds of *Arachis hypogœa* (Handbuch, viii, [2] 8). Colourless or faintly coloured oil, thinner than olive oil. Sp. gr. 0·9163. Deposits a large quantity of tallow at 3°, and solidifies to a soft mass at — 3° to — 4° (Payen & O. Henry). Solidifies completely at — 7° (Gössmann). Has an agreeable taste, resembling that of almond oil, and an odour like olive oil at 50° to 75° only. — It does not easily turn acid and is non-drying. It yields a very white and hard soap (Bouillon-Lagrange, *J. Pharm.* 8, 231). Absorbs oxygen more slowly than almond-oil. Does not solidify with mercurous nitrate. Dissolves very slightly in alcohol, but easily in ether (Payen & O. Henry, *J. Chim. méd.* 1, 437; Ostermaier, *Repert.* 98, 243; J. A. Buchner, *Repert.* 98, 251). Contains the glycerides of arachidic, palmitic, and physetoleic acids, but no stearin (Gössmann; Caldwell, *Ann. Pharm.* 101, 97).

*Oxygen-nucleus* $C^{40}H^{36}O^4.$

# Lithofellic Acid.

$$C^{40}H^{36}O^8 = C^{40}H^{36}O^4,O^4.$$
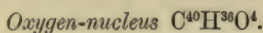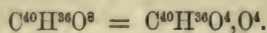
FR. GÖBEL. *Ann. Pharm.* 39, 237.
ETTLING & WILL. *Ann. Pharm.* 39, 242.
WÖHLER. *Ann. Pharm.* 41, 150; *J. pr. Chem.* 25, 50; *Pogg.* 54, 255.
HEUMANN. *Ann. Pharm.* 41, 303; *Repert.* 75, 226.
MALAGUTI & SARZEAU. *Compt. rend.* 15, 518; *Ann. Pharm.* 44, 289.
WINCKLER. *Jahrb. pr. Pharm.* 18, 376.
TAYLOR. *Phil. Mag.* 28, 192.
LUDWIG. *N. Br. Arch.* 85, 141.

*Bezoardic acid*, which name has also been given to ellagic acid (xvi, 183). — Discovered by Göbel, and investigated chiefly by him and Wöhler. — Occurs in one

of the varieties of Oriental bezoars, the gall-stones of an antelope, which consist almost entirely of this acid. Bezoars containing lithofellic acid melt when heated and dissolve in hot alcohol. Concerning these bezoars, see F. Göbell, Taylor, and Ludwig (*loc. cit.*); further Guibourt (*Rev. scient.* 14, 17. — *N. J. Pharm.* 3, 125); Hankel (*Pogg.* 55, 481).

*Preparation.* The bezoars are dissolved in boiling alcohol, and the crystals which form slowly on cooling the solution and concentrating the mother-liquor, are purified by recrystallisation, with the help of animal charcoal (Wöhler; Göbel). Or, the bezoars, after being exhausted with water, are treated for 24 hours with cold dilute ammonia; the filtrate is decolorised with animal charcoal; and the lithofellic acid is precipitated by dilute sulphuric acid and washed (Winckler). The acid precipitated from alkaline solutions requires still to be purified by crystallisation from boiling alcohol (Heumann).

*Properties.* Very small, clear, short six-sided prisms with end-faces at right angles to the sides. Rhombic prisms with oblique end-faces (Göbel). Hard and easily pulverisable. Melts at 204° (Göbel), 205° (Wöhler), and solidifies, when not heated above its melting-point, to an opaque crystalline mass. When heated a few degrees above its melting-point, it solidifies to a clear amorphous glass, which becomes electric when rubbed and melts at 105° to 110° to a viscid mass. Alcohol poured upon this amorphous acid produces a large number of fine cracks, and the acid when left in contact with a little alcohol, again becomes crystalline (Wöhler). The acid slowly excites a bitter taste in the mouth (Winckler). Has an acid reaction (Wöhler).

|  | Crystals. |  |  |  | Ettling & Will. mean. |  | Wöhler. mean. |  | Taylor. |
|---|---|---|---|---|---|---|---|---|---|
| 40 C | 240 | ........ | 70·59 | ........ | 70·39 | ........ | 70·39 | ........ | 70·18 |
| 36 H | 36 | ........ | 10·59 | ........ | 10·86 | ........ | 10·60 | ........ | 10·71 |
| 8 O | 64 | ........ | 18·82 | ........ | 18·75 | ........ | 19·01 | ........ | 19·11 |
| $C^{40}H^{36}O^8$ | 340 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Ettling & Will proposed the formula $C^{42}H^{38}O^8$. — The acid is allied to gallic acid (Göbel; Wöhler). Identical with the fellanic acid of Berzelius (*Berz. Lehrb.* 3 Aufl. 9, 273) (Heumann).

*Decompositions.* 1. Lithofellic acid boils when *heated*, evolving white fumes having a faint aromatic odour, yielding a distillate of acid oil and water, and leaving a carbonaceous residue (Göbel; Heumann). The distillate forms with potash a soap, from which hydrochloric again sets free the empyreumatic acid (Göbel). By the dry distillation of the soap, pyrolithofellic acid, $C^{40}H^{34}O^6$, is obtained (Malaguti & Sarzeau). — 2. The acid *burns* with a luminous smoky flame (Wöhler). — 3. It dissolves in *nitric acid* when heated [with fine red, afterwards yellow, colour (Taylor)], frothing up and evolving nitric oxide, and remains on evaporation as a lemon-yellow mass, which dissolves in caustic potash, and is precipitated from the solution by acids in the form of a brown friable mass (Göbel). A nitrogenous acid *Acide lithazofellique*, $C^{40}H^{28}O^{14},2NO^4$, is produced in the reaction (Malaguti & Sarzeau). — 4. The acid produces a violet-red coloration with *oil of vitriol* and *sugar*, like bile (Strecker, *Ann. Pharm.* 67, 53)

Lithofellic acid is insoluble in *water*. — It dissolves in *oil of vitriol*, from which it is precipitated by water (Wöhler) unaltered and amorphous (Taylor).

It dissolves easily in caustic *ammonia* and its carbonate, also in dilute aqueous *alkalis*, and is thrown down by acids as an amorphous precipitate, melting at 105° (Wöhler). The alkaline solution is rendered milky by sal-ammoniac (Wöhler). The ammoniacal solution leaves the acid free from ammonia on evaporation (Göbel; Wöhler). A saturated solution of the acid in caustic potash has a slightly alkaline reaction, and leaves on evaporation a clear gum, which dissolves in water, but not in caustic potash (Wöhler). When heated with a strong solution of caustic potash, lithofellic acid forms a limpid yellowish soap, which floats on the surface of the lye, and forms on cooling a solid mass resembling colophony, and easily soluble in water, alcohol, and ether (Göbel).

*Lithofellate of soda*, prepared by saponifying the acid with caustic soda, and washing the soap repeatedly with a saturated solution of salt, yields, when decomposed by hydrochloric acid, 10·4 parts of soda to 100 parts of lithofellic acid (Göbel). — Amorphous gum (Heumann).

*Baryta-salt.* — A solution of the acid in ammonia or fixed alkalis precipitates salts of baryta (Göbel; Wöhler). An alcoholic solution of the acid, mixed with water till the cloudiness at first produced disappears, does not precipitate chloride of barium or calcium (Ludwig). — On heating the acid with carbonate of baryta and evaporating, crystals are obtained, which dissolve in alcohol and separate therefrom as an oil, afterwards solidifying in a crystalline mass (Heumann).

Lithofellate of soda precipitates salts of *baryta, iron, lead, mercury, silver*, and *platinum* (Göbel). The ammonia-salt precipitates baryta-salts (Wöhler).

*Lead-salt.* — Lithofellate of potash produces with neutral lead-salts a plaster-like precipitate, containing 32 p. c. of oxide of lead (Wöhler). — Aqueous ammoniacal lithofellic acid throws down from neutral acetate of lead, a precipitate containing 41·45 p. c. of oxide of lead (Wöhler). The dazzling white precipitate thrown down by an ammoniacal alcoholic solution of the acid from neutral acetate of lead, dissolves with difficulty in water, but somewhat more freely in alcohol, and contains 49 p. c. of lead-oxide (Ettling & Will).

*Silver-salt.* — Ammoniacal nitrate of silver throws down from alcoholic lithofellic acid, bulky flocks, which disappear on addition of alcohol. By evaporating the solution, long light needles are obtained, which blacken on exposure to light, and contain, like the flocks, 25·43 p. c. of silver-oxide (Ettling & Will). Wöhler obtained from a solution of the silver-salt, a creamy non-crystalline pellicle containing 25 p. c. of oxide of silver.

Lithofellic acid dissolves freely in strong *acetic acid*, and crystallises on evaporating the solution (Wöhler). — It dissolves in 6·5 parts of boiling 90 p. c. *alcohol* and in 29·4 parts at 20° (Göbel), from which it is precipitated by water. It is soluble in 47 parts of boiling, and 444 parts of cold absolute *ether* (Göbel).

*Oxygen-nucleus* $C^{40}H^{34}O^6$.

# Flocks from Rottlera tinctoria.

$$C^{40}H^{34}O^8 = C^{40}H^{34}O^6,O^2.$$
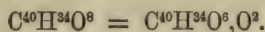
When the hairs and glands which cover the fruit of *Rottlera tinctoria* (the kamala of commerce) are exhausted with boiling alcohol, the tincture, on cooling, deposits flocks, which may be obtained nearly colourless by repeated crystallisation. The mother-liquor retains in solution a resinous colouring matter.

Granular, non-crystalline flocks, not precipitable by salts of lead or silver. — Insoluble in water, but slightly soluble in ether and cold alcohol (Anderson, *Pharm. Centr.* 1855, 373).

|  |  |  |  |  | Anderson. *mean.* |
|---|---|---|---|---|---|
| 40 C | 240 | ............ | 71·00 | ............ | 70·78 |
| 34 H | 34 | ............ | 10·05 | ............ | 10·45 |
| 8 O | 64 | ............ | 18·95 | ............ | 18·77 |
| $C^{40}H^{34}O^8$ | 338 | ............ | 100·00 | ............ | 100·00 |

*Resinous colouring matter of Rottlera.* — Remains on evaporating the mother-liquor of the flocks just described, as a dark-red resin melting at 100°, purified by solution in ether. — It is insoluble in water, but soluble in all proportions in alcohol and ether, and is thrown down by neutral acetate of lead as a deep orange-red precipitate. A solution in aqueous carbonate of soda dyes silk a fine permanent orange (Anderson).

|  |  |  |  |  | Anderson. *mean.* |
|---|---|---|---|---|---|
| 60 C | 360 | ............ | 71·71 | ............ | 71·35 |
| 30 H | 30 | ............ | 5·97 | ............ | 6·29 |
| 14 O | 112 | ............ | 22·32 | ............ | 22·36 |
| $C^{60}H^{30}O^{14}$ | 502 | ............ | 100·00 | ............ | 100·00 |

*Resins from Rottlera tinctoria* (Kamala). — See xiv, 520. Leube did not succeed in preparing Anderson's rottlerin. — The extract of kamala prepared by extraction with ether, breaks up when heated with cold alcohol, after previous boiling with water, into an easily soluble and a sparingly soluble resin, both of which are brittle and reddish-yellow, the easily soluble melting at 80°, and the sparingly soluble at 191°. Both resins dissolve in caustic potash with fine red colour, and in ammonia and carbonate of ammonia, from which they are precipitated by acids. They form oxalic acid with nitric acid, and do not yield sugar with dilute sulphuric acid. The easily soluble resin contains at 60°, on the average, 68·53 p. c. C., 6·97 H., and 24·50 O. ( = $C^{30}H^{18}O^6$); the sparingly soluble, at 150°, 51·18 p. c. C., 6·21 H., and 42·61 O. ( = $C^{16}H^{12}O^{10}$) (Leube, *Pharm. Viertelj.* 9, 321).

*Oxyazo-nucleus* $C^{40}N^2H^{28}O^{10}$.

# Emetine.

? $C^{40}N^2H^{30}O^{10} = C^{40}N^2H^{28}O^{10},H^2$.
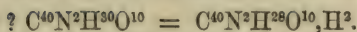
PELLETIER & MAGENDIE. *Ann. Chim. Phys.* 4, 172; *Schw.* 19, 440; Complete: *J. Pharm.* 3, 145.
PELLETIER & DUMAS. *Ann. Chim. Phys.* 24, 180.
PELLETIER. *J. Pharm.* 14, 200.
MERCK. *N. Tr.* 20, 1, 134.
LANDERER. *Repert.* 52, 211.
REICH. *N. Br. Arch.* 113, 193.

Prepared by Pelletier in 1816 in an impure, and in 1821 in the pure state. — Occurs in the Ipecacuanha roots of *Cephaëlis Ipecacuanha, Richardsonia scabra;* also of *Psychatria emetica, Jonidium Ipecacuanha,* and *Euphorbium Ipecacuanha.* — Pleischl (*Das chem. Labor. zu Prag,* 1820) and Buchholz (*Taschenb.* 1818, 97) describe a soft resin of Ipecacuanha.

*Preparation.* The root-bark is exhausted with ether to remove soft resin, and then boiled with alcohol; the tincture is evaporated, and the residue dissolved in water, whereupon wax separates. The aqueous solution is freed from gallic acid (ipecacuanhic acid, xv, 523) by digesting it with carbonate of baryta; the emetine is precipitated with basic acetate lead; the precipitate is washed, and decomposed under water by hydrosulphuric acid; and the liquid is filtered and evaporated. — The impure emetine thus obtained is boiled with water and excess of calcined magnesia; the precipitate is washed with a very little cold water to remove colouring matter, then dried and boiled with alcohol; the solution is filtered and evaporated; and the residue is dissolved in aqueous acid and decolorised by animal charcoal, after which the emetine is precipitated by magnesia and again extracted by alcohol (Pelletier). The water with which the magnesian precipitate is washed, and probably also the filtrate from the lead-precipitate, still contain a little emetine (Pelletier). See below.

2. The bruised root is boiled with water; the extract is evaporated to dryness, and the residue exhausted with alcohol. The tincture is filtered, freed from alcohol by distillation, and again evaporated to dryness; and the residue is exhausted with dilute hydrochloric acid. The solution thus obtained is precipitated with chloride of mercury; the precipitate is washed with cold water and dissolved in alcohol; and the mercury is thrown down by the addition of sulphide of barium. Excess of baryta is then removed by sulphuric acid; the solution is diluted with water and distilled to remove alcohol; and the emetine is precipitated by ammonia and washed with cold water (Merck).

Landerer precipitates the acetic extract of ipecacuanha with magnesia, and after washing and drying the precipitate, exhausts it with alcohol. The emetine which remains on evaporating the alcohol is purified by dissolving it repeatedly in acetic acid, decolorising the

solution with animal charcoal, and precipitating with magnesia. — Reich exhausts the coarsely powdered root with warm alcohol, mixes the tincture with neutral acetate and basic acetate of lead in succession, whereby ipecacuanhic acid is thrown down; then filters the solution, distils off the greater part of the alcohol, and dilutes the residue with water, which precipitates resin. After removing the resin, and also the lead, by means of hydrosulphuric acid, the emetine is precipitated by tannic acid; the precipitate is triturated with oxide of lead, dried, and boiled with alcohol, which takes up the emetine and leaves it behind on evaporation. The product may be purified by again precipitating it with tannic acid and decomposing the precipitate, and lastly by exhausting it with ether. — The yield is ¼th to ⅓rd per cent. (Pelletier).

*Properties.* White, inodorous powder, having a slightly bitter taste (Pelletier). According to Landerer, cubic crystals. Has a strongly acid reaction according to Pelletier, but according to Landerer, turmeric is not affected by it, and litmus only slightly. Melts at 50° (Pelletier). It acts as an emetic, and is poisonous in large doses. — Without action on polarised light (Buignet, *Compt. rend.* 52, 1085).

|  |  |  |  |  | Dumas & Pelletier. | | Reich. |
|---|---|---|---|---|---|---|---|
| 40 C ................ | 240 | ........ | 63·49 | ........ | 64·57 | ........ | 63·11 |
| 2 N ................ | 28 | ........ | 7·40 | ........ | 4·30 | ........ | 6·11 |
| 30 H ................ | 30 | ........ | 7·93 | ........ | 7·77 | ........ | 7·99 |
| 10 O ......  ........ | 80 | ........ | 21·18 | ........ | 23·36 | ........ | 22·79 |
| C⁴⁰N²H³⁰O¹⁰ .... | 378 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

The above is Reich's formula. According to Pelletier & Dumas, it is C³⁵NH²⁵O⁹; according to Fehling (*Handwörterb.* 2, 2, 3, 777) probably C³⁶NH²⁵O¹⁰. The above formula requires verification.

*Decompositions.* 1. Emetine melts when *heated*, like wax, takes fire at a stronger heat, evolving dense fumes, and burns (Merck; Reich). — 2. Its *salts* are violently decomposed by the *electric current* (Hlasiwetz & Rochleder, *Wien. Akad. Ber.* 5, 447). — 3. A solution in 400 parts of acidulated water assumed a saffron-yellow colour on passing chlorine into it for ten minutes, and deposited a slight precipitate; the emetine, however, was not quite pure (Lepage, *J. Pharm.* 26, 140). — 4. Emetine acquires a brownish-yellow colour in vapour of *iodine*, and a greenish-yellow brown in vapour of *bromine* or *chloride of iodine* (Donné). — 5. According to Guy, *oil of vitriol* does not colour emetine, but according to Merck, it produces a dirty olive-green coloration. — 6. *Nitric* acid colours it yellowish-brown (Guy); brown-red, and resinises it (Merck). — 7. Strong *hydrochloric acid*, boiled with *emetine*, does not produce a splitting up, and does not form any substance having a reducing action on an alkaline solution of copper; neither does unchanged emetine cause a separation of cuprous oxide (Reich).

*Combinations.* Air-dried emetine loses 2·4 p. c. of *water* at 100° (Reich). — It dissolves with difficulty in cold, and somewhat more freely in hot water (Pelletier). It is insoluble in *ammonia-water* (Merck).

*With Acids.* — Emetine dissolves in all acids [including acetic acid (Merck)], which it neutralises. The *salts* are not susceptible of crystallisation, with some exceptions in presence of excess of acid (Pelletier). According to Landerer, the phosphate crystallises. — They are precipitated by ammonia and carbonate of ammonia, and by caustic alkalis and their carbonates and bicarbonates, also by magnesia, the precipitates not being soluble in excess of the precipitants (Planta). In the pure state they are not precipitated by basic acetate of lead (Pelletier).

*Phosphate of soda* does not precipitate hydrochlorate of emetine. *Tincture of iodine* produces a carmine-red, *iodic acid* a yellow, iodide of potassium a yellowish-white precipitate (Planta). *Phosphomolybdic acid* throws down pale-yellow flocks (Sonnenschein), *iodhydrargyrate of potassium*, a yellowish-white [amorphous (Dellfs)] powder, insoluble in hydrochloric acid, *mercuric chloride*, a white powder sparingly soluble in hydrochloric acid, and insoluble in sal-ammoniac ; *terchloride of gold*, a flesh-coloured, *bichloride of platinum*, a yellowish-white, *chloride of iridium and sodium*, an ochre-yellow precipitate. — *Sulphocyanide of potassium* produces a pulverulent, yellowish-white precipitate (Lepage ; v. Planta). *Oxalates* and *tartrates* of the alkalis do not precipitate salts of emetine (Pelletier). *Croconate* of emetine is yellow, indistinctly crystalline, and soluble in water and alcohol ; the *rhodizonate* is hyacinth-red (Heller). — Hydrochlorate of emetine yields with *picric acid* a sulphur-yellow powder (Merck ; v. Planta). It is rendered turbid by a little *tincture of galls*, whereupon a drop of hydrochloric acid produces a dense, whitish precipitate, which dissolves in more hydrochloric acid (v. Planta). The precipitate produced by infusion of galls does not act as an emetic ; it is nearly insoluble in water, but soluble in aqueous alkalis (Pelletier).

Emetine dissolves very easily in dilute and in absolute *alcohol*, but is insoluble in *ether* and in *oils* (Pelletier ; Merck).

### Appendix to Emetine.

*Violine.* — *Violenemetine.* Occurs, according to Boullay, in all parts of the *Viola odorata*. — An alcoholic extract of the dried root is freed from chlorophyll and fat by means of ether, and the residue is boiled with dilute sulphuric acid (whereby acetic acid is volatilised), evaporated to dryness with excess of hydrated oxide of lead, and exhausted with alcohol of 40°. The alcoholic solution, when evaporated, leaves violine, from which a little colouring matter may be extracted by a small quantity of strong alcohol. Violine forms a pale-yellow, bitter powder, which melts when heated, and burns like resin ; it is more soluble in water, but less soluble in alcohol than emetine, and insoluble in ether. It combines with acids, without forming distinct salts therewith (Boullay, *Mem. de l'Acad. de Méd.* 1828, 1, 417 ; abstr. *Repert.* 31, 37).

Torosiewicz distinguishes as *melonenemetine*, an aqueous extract of melon root, which has been but little investigated.

# 1. Resins.

### On Resins in general.

The older chemists distinguished by the general name *resin*, substances insoluble in water, generally soluble in alcohol, for the most part uncrystallisable, and softening or melting when warmed, such substances being either :

a. *Secretions of Plants*, generally exuding from the plant, and hardening in the air. They are, as a rule, mixtures, sometimes containing considerable quantities of gum, mucus, or volatile oil, and in such cases distinguished as *Gum-resins*, or as natural *Balsams*. — Related to the resins separated from living plants are the *Fossil* or *Earth resins*.

Or b. *Substances extracted from plants* with help of alcohol, not separable into simpler constituents, and therefore regarded as simple organic compounds.

The uncrystallisable coloured products obtained by the decomposition of volatile oils in the air, or by nitric acid ; by the drying up of drying fatty oils ; by the decomposition of alcohol, aldehyde, and other organic compounds by potash ; and by the dry distillation of many organic compounds, are also designated as resins.

Volatile oil, when mixed with resin, is removed by exposure to the air, by boiling with water, or by melting the resin. — Hot alcohol or ether extracts the resin from vegetable organs ; the solutions deposit most of the wax or fat on cooling, and, when mixed with water and distilled, leave the resin as residue.

The products thus obtained frequently contain also acid, fat, volatile oil, or colouring matter, &c. ; some of them are further decomposible into resins of different properties.

Resins are transparent or translucent, colourless, yellow, brown, or otherwise coloured, either hard and brittle, and in that case sometimes crystalline (*hard resins*), or greasy (*soft resins*), or elastic (*caoutchouc*). When warmed they soften or melt, generally without decomposition, to a thick viscid liquid, usually thicker than melted fat. They are inodorous, sometimes tasteless, sometimes having a bitter or acrid taste (*mild* or *acrid resins*). When dissolved in alcohol, they in some cases redden litmus, without yielding a peculiar acid (*acid resins*), and in other cases are without action upon it (*neutral resins*). — They are more easily inflammable than fats, and burn with a bright, very smoky flame. — They are insoluble in water. They are mostly capable of combining with salifiable bases. Their solutions in caustic potash or soda leave on evaporation, amorphous masses, the *resin-soaps*, frequently precipitable from their aqueous solutions by excess of potash. The compounds with metallic oxides, obtained by double decomposition, are generally insoluble in water. Neutral resins are insoluble, or nearly so, in alkalis.

Most resins are freely soluble in cold alcohol, but a few are nearly insoluble, or soluble only in the hot liquid ; caoutchouc is insoluble.

The alcoholic solutions are turned milky by water, and precipitated more completely by mineral acids. On exposure to the air, they leave the resins behind : *Spirit-varnish.* Most resins are soluble in ether ; volatile oils also dissolve them, and on exposure to air leave first a balsam-like mass, and then the resins : *Turpentine varnish.* Resin may be melted together with fat ; the solution in drying-fat hardens in the air : *Fatty varnish.*

Unverdorben has attempted a classification of the resins. See also Johnston on the formulæ of the resins, and Heldt on the laws of the formation of resins.

HATCHETT. *N. Gehl.* 1, 555.
BOUILLON-LAGRANGE & VÖGEL. *Ann. Chim.* 72, 72.
PELLETIER. *J. Phys.* 79, 275. — *Ann. Chim.* 79, 90 ; 80, 38. — *Bull. Pharm.* 3, 381 ; 4, 502.
BRACONNOT. *Ann. Chim.* 68, 19 and 66.
BONASTRE. *J. Pharm.* 9, 178 ; 10, 1 ; 12, 492.
UNVERDORBEN. *N. Tr.* 8, 1, 21 ; *Pogg.* 7, 311 ; 8, 40 and 407 ; 11, 28, 230 and 393 ; 14, 116.
BERZELIUS. *Pogg.* 10, 252 ; 12, 419 ; 13, 78.
DEVILLE. *N. Ann. Chim. Phys.* 3, 151.
JOHNSTON. *Lond. Edinb. Phil. Mag.* 13, 474 ; 14, 95 and 340 ; *J. pr. Chem.* 17, 157.
ROSE. *Pogg.* 53, 384.
HELDT. *Ann. Pharm.* 63, 50.

The following pages contain, generally in alphabetical order, first the resins and balsams containing benzoic and cinnammic acids, which exude from living plants ; then the resins free from benzoic acid, and the earth-resins ; and lastly those extracted from plants. The list includes also a few of the bodies allied to resins.

## A. *Resins containing Benzoic or Cinnamic acid.*

1. BENZOÏN. — *Asa dulcis.* From *Styrax Benzoïn.* Irregular granules or tears of a reddish-yellow colour without, and milk-white within ; brittle, with conchoïdal fracture and fatty lustre ; also irregular porous masses, of a dirty red-grey to brown colour, and slightly shining fracture, in which the white granules are disseminated in greater or lesser number. — Sp. gr. 1·003 (Pfaff), 1·092 (Brisson). It has an agreeable odour, especially when warmed or rubbed, and a sweetish-acrid balsamic taste.

Benzoïn contains traces of volatile oil [sometimes an oil which when treated with chlorine yields chloride of benzoyl (Frémy)], benzoic acid varying in amount from 12·5 to 19·8 p.c., a resin soluble in ether, and a second resin insoluble in that liquid (Buchholz ; Stoltze). The white granules consist almost exclusively of the resin soluble in ether, whilst the brown benzoïn consists chiefly of the insoluble resin (Stoltze, *Berl. Jahrb.* 25, 1, 55). See below. Some varieties of benzoïn, especially an almond benzoïn from Sumatra, contain cinnamic and benzoic acids (Kolbe and Lautemann, *Ann. Pharm.* 119, 136 ) ; such resin

of the first quality contains only cinnamic acid : the brown Sumatra resin contains only benzoic acid (Aschoff, *N. Br. Arch.* 107, 153 ; *Chem. Centr.* 1861, 650).

The resins of benzoïn contain a group of substances belonging to the benzoyl series, and a second belonging to the phenyl series, the derivatives of which occur in the products of decomposition. 1. In the dry distillation of benzoïn free from benzoic acid, a fatty unctuous body, probably the odorous principle, is obtained, together with benzoic and carbolic acids (E. Kopp). Cahours (*N. Ann. Chim. Phys.* 3, 192) obtained by the dry distillation of benzoïn free from acid, an oil, $C^{36}H^{18}O^4$, resembling benzoate of ethyl, which was completely converted into benzoic acid by hydrate of potash. Umbelliferone is not formed in the dry distillation (Sommer). — 2. Chromic acid forms oil of bitter almonds and benzoic acid, together with carbonic and formic acids. — 3. Nitric acid produces a violent frothing, with evolution of red fumes, and forms a brittle, porous, very bitter, orange-yellow mass, from which picric and benzoic acids are produced by the continued action of the nitric acid, whilst hydrocyanic acid, oil of bitter almonds, and benzoic acid distil off. — 4. Oil of vitriol dissolves the resins of benzoïn with carmine-red colour, forming a solution from which water throws down a copious violet precipitate ; it yields a soluble lime-salt when saturated with that base (E. Kopp, *Compt. rend.* 19, 1269).

Benzoïn, purified by boiling with carbonate of potash, dissolving the residue in alcohol, distilling, and precipitating with water, yields when melted with hydrate of potash, benzoic acid, paraoxybenzoic acid, $C^{14}H^6O^6$, protocatechuic acid, $C^{14}H^6O^8$, (also a compound of these two acids in equal numbers of atoms), pyrocatechin, acetic acid, propionic acid, and butyric acid. Small quantities of a crystallisable acid (probably $C^{18}H^8O^{10}$) which dissolves with difficulty in dilute alcohol and assumes a fine red colour with sesquichloride of iron, are also obtained (Hlasiwetz and Barth, *Ann. Pharm.* 134, 265).

Benzoïn is slightly soluble in *ammonia*, but more freely soluble in boiling *caustic potash*, with brown colour. Boiling *water*, *milk of lime*, and aqueous *alkaline carbonates* extract benzoic acid from it. See below. It is soluble in cold *acetic acid*. *Alcohol* forms a reddish-brown solution, precipitable by acids and water : *ether* also dissolves it (Brande) (See above). Cold *creosote* dissolves it completely (Reichenbach).

The yellowish-white almonds of benzoïn melt at about 93°, and solidify on cooling to a colourless, transparent, brittle resin, which turns brown when more strongly heated, with liberation of benzoic acid. After being kept in a semi-fluid state for 20 hours at 93°, it contains 72·01 p. c. C., 6·67 H.; and 21·32 O. (deducting 0·23 p. c. of ash) (Johnston, *Phil. Trans.* 1840, 369). — White benzoïn soluble in ether without residue, and melting at 95°, contains 72·23 p. c. C., 6·80 H., and 20·97 O. (Schrötter, *Pogg.* 59, 71).

*Separation of the resins of Benzoïn.* — A. *According to Stoltze.* —An alcoholic solution of benzoïn is neutralised with carbonate of soda and evaporated with water, the separation of the resin being promoted by the addition of carbonate of soda. The precipitate is washed with water and treated with ether, which dissolves one resin and leaves the other undissolved.

*a.* The *resin soluble in ether* is pale-yellow, friable, neutral, easily fusible, with agreeable odour, and does not yield benzoic acid when decomposed at a higher temperature. It dissolves in oil of vitriol, with dark-red colour. When precipitated from an alcoholic solution by water and diluted, it remains suspended, as a milky liquid, which becomes clear only when left at rest for several days, but immediately on addition of mineral acids, acetic acid, or Glauber's salt. — The resin dissolves in warm caustic potash: it is precipitated from its alcoholic solution by neutral acetate of lead: easily soluble in strong acetic acid, from which it is precipitated by water. — *b.* The *resin insoluble in ether* is brown, friable, easily fusible, and insoluble in volatile and fatty oils (Stoltze).

B. *According to Unverdorben and van der Vliet.* — Benzoïn boiled with aqueous carbonate of soda gives up to that liquid benzoic acid and a little gamma-resin : from the residue ether extracts alpha-resin, whilst beta-resin soluble in alcohol remains behind. These three resins yield the same products when heated with hydrate of potash (Hlasiwetz & Barth).

a. *Alpha-resin.* — Freed from volatile constituents by warming. Pale-brown. Insoluble in aqueous ammonia or carbonate of soda, but easily soluble in caustic potash, alcohol, and oil of cumin. Its alcoholic solution precipitates alcoholic neutral acetate of lead, but not alcoholic acetate of copper (Unverdorben). It contains, on an average, 71·85 p. c. C., 7·19 H., 20·96 O. [72·74 C., 7·33 H., 19·93 O (Mulder) ] ; in the lead-salt 16·44 p. c. of oxide of lead, the residue consisting of 71·90 p. c. C., 7·08 H., and 21·02 O., (van der Vliet).

b. *Beta-resin.* — After the extraction of the alpha-resin the residue contains beta-resin, a compound of alpha-resin with carbonate of soda, and the impurities of the benzoïn. Its solution in boiling alcohol deposits the compound of alpha-resin with carbonate of soda on cooling ; the filtrate yields on evaporation the beta-resin, which is boiled with water containing hydrochloric acid (van der Vliet). — The beta-resin is insoluble in ether, but easily soluble in caustic potash, from which it is precipitated by a large quantity of potash. It behaves in other respects like the alpha-resin (Unverdorben).—Contains, on an average, 70·43 p. c. C., 6·70 H., 22·87 O. (van der Vliet) ; 71·41 p. c. C., 6·88 H., and 21·71 O. (Mulder) ; in the lead-salt, 25·46 p. c. of oxide of lead, the residue containing 71·74 p. c. C., 6·28 H., and 21·98 O. (van der Vliet).

c. *Gamma-resin.* Extracted from benzoïn by boiling with carbonate of soda, precipitated from the solution by hydrochloric acid, and purified by boiling with water. — The gamma-resin is formed from the alpha and beta-resins in moist air, inasmuch as these latter become thereby soluble in aqueous carbonate of soda. — It dissolves in aqueous ammonia, in caustic potash, from which it is precipitated by further addition of potash, in alcohol, and with difficulty in ether and oil of cumin. It behaves in the same manner as the α-resin towards neutral acetate of lead and acetate of copper. — Contains 74·44 p. c. C., 8·49 H., and 17·07 O., (van der Vliet) ; 73·76 C., 8·67 H., 17·67 O., (Mulder) ; in the lead-salt 31·28 p. c. of oxide of lead (van der Vliet, *J. pr. Chem.* 18, 411 ; *Ann. Pharm.* 34, 177 ; Unverdorben, *Pogg.* 17, 179). See also Frémy

(*Ann. Chim. Phys.* 70, 203); Dulong (*J. Pharm.* 12, 33). On the formulæ of the resins of benzoïn, see also Ludwig (*N. Br. Arch.* 123, 21).

C. *According to Johnston.* — *a.* When picked benzoïn is freed from benzoic acid by repeated boiling with water and with dilute and strong carbonate of potash, a red-brown residue is left, which is completely soluble in alcohol and ether, and yields no sublimate of benzoic acid when heated in a narrow tube. It contains, on an average, 71·61 p. c. C., 7·49 H., and 20·90 O., corresponding to the formula $C^{40}H^{24}O^8$. — *b.* A similar red-brown resin is obtained by boiling benzoïn with milk of lime, washing with a large quantity of boiling water, decomposing the un-dissolved compound of resin and lime with boiling hydrochloric acid, dissolving the precipitated resinous acid in alcohol, and evaporating. It evolves a volatile oil when heated to about 120°, and contains 70·00 to 72·23 p. c. C., 7·38 to 7·63 H., 22·62 to 20·14 O., corresponding to the formula $C^{40}H^{24}O^8$ or $C^{40}H^{24}O^9$ (Johnston). — *c.* When the last wash-waters of the lime-compound are precipitated by hydrochloric acid, grey-white flocks are obtained, which contain 73·11 p. c. C., 9·21 H., and 17·68 O., corresponding to the formula $C^{40}H^{30}O^7$ (Johnston).

*d.* Strong solution of caustic potash, added to the cold alco-holic solution of benzoïn, turns the liquid darker, and throws down a grey precipitate, which dissolves in a larger quantity of caustic potash, and is again precipitated by tincture of benzoïn. If the precipi-tates are collected, washed with boiling water, which takes up but little, again dissolved in caustic potash, precipitated by hydrochloric acid, and washed with hot water, a grey resinous powder is obtained, which is deposited almost entirely from its solution in boiling alcohol or ether on cooling. It is still a mixed substance, from which alcohol takes up a portion containing 71·73 p. c. C., 7·33 H., and 20·94 O., corresponding to the formula $C^{40}H^{24}O^8$, after which ether extracts a second portion containing 71·00 p. c. C., 6·77 H., and 22·23 O., cor-responding to the formula $C^{40}H^{22}O^9$. — *e.* The solution which has been precipitated by potash throws down, on dilution with water, a slight precipitate, after the removal of which the filtrate is to be precipi-tated by hydrochloric acid. The precipitate thus obtained is washed with hot water, dissolved in alcohol, and recovered from the solution by evaporation. After drying for a short time at 93°, it contains 73·02 p. c. C., 9·16 H., and 17·82 O.; on more prolonged drying the percentage of carbon decreases to 69·77.

Alcoholic neutral acetate of lead throws down from an alcoholic solution of benzoïn, a slight precipitate, containing 24·86 p. c. of lead-oxide: the filtrate yields, on addition of ammonia, a further precipi-tate containing 41·41 p. c. This last, when boiled with hydrochloric acid, furnishes a resin, which, after solution in alcohol and evaporation, contains 69·17 p. c. C., 7·60 H., and 23·23 O., corresponding to the formula $C^{40}H^{26}O^{10}$ (Johnston, *Phil. Trans.* 1840, 369). According to Unverdorben, neutral acetate of lead does not precipitate alcoholic benzoïn.

2. YELLOW RESIN FROM BOTANY BAY. — From *Xanthorrhœa hastilis.* Of a darker reddish-yellow than gamboge, frequently covered with a greenish-grey crust. Brittle, of shining fracture, triturable to a greenish-yellow powder. Does not stick to the teeth. Tastes sour and

aromatic, and has an agreeable balsamic odour.　Contains a very small quantity of an agreeably-smelling volatile oil; a resin soluble in alcohol and ether, and also in alkalis and baryta- and lime-water; a little benzoic acid, and bassorin (Laugier, *Ann. Chim.* 76, 265).　Tromms-dorff (*Taschenb.* 1826, 1) distinguishes two, Widmann (*Repert.* 22, 198) three resins. — Its solution in ether or alcohol leaves on evaporation a dark resin, containing, at 120°, 66·98 p. c. C., 5·73 H., and 27·29 O., corresponding to the formula $C^{40}H^{20}O^{12}$, and almost entirely precipitable from its alcoholic solution by water, even in presence of a large quantity of ammonia (Johnston, *Phil. Trans.* 1839, 292).

The resin melts at a moderate heat, and afterwards burns with smoky flame and an odour of storax. — When submitted to *dry distillation*, it yields a large quantity of carbolic acid in the form of an acid heavy oil, and a little light oil, having the odour of a mixture of benzene and cinnamene [no umbelliferone (Sommer)]. — *Nitric acid* acts violently upon the resin, even in the cold, and dissolves it with dark-red colour; the further action of the acid produces a large quantity of picric acid (xi, 211), together with a little nitrobenzoic acid and oxalic acid (Stenhouse). — The brown-red solution of the resin in aqueous *alkalis* throws down, when neutralised with hydrochloric acid, a dark brown brittle mass, whilst the acid liquid retains in solution cinnamic acid and a little benzoic acid (Stenhouse, *Phil. Mag.* 28, 440; *Ann. Pharm.* 57, 84).

The resin gives up to boiling water benzoic acid and gum.　It dissolves in oil of vitriol, forming a pale brown solution, which is precipitated of a violet-red by water.　It colours acetic acid yellow, without dissolving in it to any great extent, and dissolves easily in alcohol, ether, some volatile oils, and partially in fatty oils, forming in all cases fine yellow solutions (Widmann; Lichtenstein).

3. DRAGON'S BLOOD. — Occurs in commerce in three different varieties, namely, Oriental (from *Calamus Draco* and other species), Canary (from *Dracæna Draco*), and American (from *Pterocarpus Draco*.　Handbuch, viii [2], 12), the first of which is further distinguished as *Sanguis Draconis in baculis, in lacrymis,* and *in massis.* — The resin is reddish-brown in mass, blood-red in powder, opaque, brittle, of dull fracture.　Sp. gr. 1, 196.　Inodorous and tasteless.　Has an odour of benzoïn when heated. — Contains fat, benzoic acid [Hempel (*Ann. Pharm,* 59, 321) found neither benzoic nor cinnamic acid], oxalic acid, phosphate of lime, and 90 p. c. of colouring matter, which is precipitated from the alcoholic solution by sulphuric acid (Melandri's *Dracin;* Herberger's *Drachenblutstoff*). — According to Melandri (*Br. Arch.* 25, 193), dragon's blood dissolves gradually in warm water. — It dissolves, for the most part, in alkalis (Herberger), and slightly in lime-water, the fine red solutions being precipitated of a yellow colour by acids. — It dissolves easily with purple colour in alcohol, in acetic acid, less easily in ether, and in fatty and volatile oils [not in castor oil (Stickel)] (Herberger, *Repert.* 37, 17), easily in fusel oil, less freely in valerianic aldehyde, and still less in valerianic acid and valerate of amyl (Trautwein, *Repert.* 91, 29).

Dragon's blood, when submitted to dry distillation, melts, gives off acid water together with acetone and benzoic acid up to 210°, swells up, evolves carbonic acid and carbonic oxide with dense white fumes, and yields a distillate of black-red oil, whilst a large quantity of carbon remains behind.　The oil contains dracyl (toluol, iv, 226) and draconyl

[styrol, which is transformed into metastyrol (xiii, 6) by rectification (Hofmann & Blyth), and probably occurs as metastyrol in dragon's blood (Kovalewsky, *Ann. Pharm.* 126, 69)]. After distilling off these two substances at a temperature below 180°, there passes over an oily mixture of benzoic acid with an oxygenated oil heavier than water, and turning red and black in the air, from formation of benzoic acid and a peculiar liquid (Glenard & Boudault, *Compt. rend.* 17, 503; *N. J. Pharm.* 4, 274; *Ann. Pharm.* 48, 343. — *Compt. rend.* 19, 505; *N. J. Pharm.* 6, 250).

Dragon's blood is violently acted upon by *nitric acid* of sp. gr. 1·34 when warmed therewith, becoming very hot, and dissolving completely in 6 or 8 parts of the liquid, with formation of oxalic acid, and perhaps a trace of picric acid. — Nitric acid, diluted with an equal volume of water, dissolves dragon's blood gradually on boiling, vapours smelling of nitrobenzene and hydrocyanic acid passing over, and a non-volatile, pulverulent acid, together with a sublimable acid, probably nitrobenzoic acid, being formed (Blumenau, *Ann. Pharm.* 67, 127). Böttger & Will (*Ann. Pharm.* 58, 274) likewise obtained only benzoic acid (no styphnic acid) by the action of nitric acid. — Alcoholic dragon's blood reduces *nitrate of silver* on standing (Johnston). — Dragon's blood melted with *caustic potash*, yields phloroglucin and protocatechuic acid (Hlasiwetz & Pfaundler, *Wien. Acad. Ber.* 50, 52). Hlasiwetz & Barth afterwards obtained the following results: dragon's blood, purified by dissolving it in alcohol, distilling off the alcohol, and precipitating the residue with water, yields, when melted with caustic potash, (1) acetic acid (or butyric or propionic acid); (2) benzoic acid; (3) paraoxybenzoic acid; $C^{14}H^6O^6$, (4) a compound of paraoxybenzoic with protocatechuic acid in equal numbers of atoms; (5) phloroglucin; (6) a difficultly soluble acid, $C^{18}H^8O^{10}$, which is also obtained from benzoïn (p. 385); (7) oxalic acid; and (8) a small quantity of microscopic needles, corresponding to the formula $C^{18}H^{10}O^6$. Dragon's blood in tears and that in sticks yield the same products, but in different proportions, in the one case a large quantity of phloroglucin and but little paroxybenzoic acid being produced, and in the other case a small quantity of phloroglucin, but a large quantity of paraoxybenzoic acid, either free or combined with protocatechuic acid (Hlasiwetz & Barth, *Ann. Pharm.* 134, 283).

Johnston (*Phil. Trans.* 1839, 134; 1840, 384) examined two varieties of dragon's blood, one comparatively pure, the other mixed with vegetable remains.

α. When the purer dragon's blood, occurring in commerce in sticks, is digested with alcohol, and the filtered liquid is evaporated over the water-bath, there remains a nearly black residue, of a splendid red colour, translucent in thin layers, and triturable to a dark red powder. After evaporating the solution at 82°, the residue swells up when heated to 100°, giving off astringent vapours; at a temperature of 93° it loses the whole of the alcohol or ether in 12 hours, and dissolves completely in alcohol, even after drying at 138° (analyses *a — c*). — β. When the same dragon's blood is dissolved in ether, and the filtrate is evaporated, the residue exhibits a like composition, *d*, whether dried for 12 hours at 66° or 88°, or for 6 hours at 100°. — γ. The dragon's blood occurring in larger pieces, mixed with vegetable remains, but probably less altered by artificial processes, gives up to alcohol the resin *e*, to ether the resin *f*, both of which were analysed after drying for 12 hours at 88°. These resins are $C^{40}H^{21}O^8$ or $C^{40}H^{20}O^9$.

*Analyses by Johnston.*

|   | a. at 100°. | | b. at 104°. | | c. at 138°. | | d. | | e. | | f. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C | ........ | 70·93 | .... | 70·80 | .... | 72·35 | .... | 72·15 | .... | 73·16 | .... | 72·91 |
| H | ........ | 5·98 | .... | 6·11 | .... | 6·21 | .... | 6·10 | .... | 6·40 | .... | 6·66 |
| O | ........ | 23·09 | .... | 23·09 | .... | 21·44 | .... | 21·75 | .... | 20·44 | .... | 20·43 |
|   |  | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 |

4. PERU BALSAM. — From *Myroxylon peruiferum*. Occurs in commerce in the solid and in the fluid state. It is dark red-brown, transparent, and of spongy consistence. Sp. gr. 1·15 (Lichtenberg; Stoltze), 1·1475 (Brandes & Reiche). It smells like vanilla, and tastes at first mild, afterwards bitter and aromatic, producing a pricking sensation on the tongue and throat. When taken internally, it occasions the formation of hippuric acid, and the urine acquires a blood-red colour on being heated with hydrochloric acid (Wöhler & Frerichs, *Ann. Pharm.* 65, 339).

Peru balsam contains cinnameïn (xiii, 283) and frequently also styracin (xiii, 286), cinnamic acid (xiii, 268), a resin easily soluble, a second resin difficultly soluble in alcohol, and extractive matter soluble in water.

The balsam deposits crystals of cinnamic acid (xiii, 269) on prolonged standing. — When distilled with water it yields little or no volatile oil (Lichtenberg). — When it is heated to 100° a trace only of oil and acid are obtained; at 287° the balsam boils and yields first a yellow, then a brown oil, together with a little acid, water, carbonic acid, and combustible gas (Lichtenberg). By dry distillation, water, oil, and a large quantity of cinnamic acid are obtained (Scharling). Without a wick, the balsam burns only at a high temperature, but with a wick it burns easily, with bright smoky flame. — Nitric acid dissolves it with violent action and formation of hydrocyanic acid (Hatchett). — When mixed with cold oil of vitriol, the balsam becomes hot and evolves sulphurous acid, forming a dark-brown mixture, which yields a sublimate of benzoic acid when heated (Stoltze; Hatchett). — On dropping the balsam into boiling concentrated solution of chloride of zinc, water and a little cinnamic acid pass over, together with a light and a heavy brown empyreumatic oil, which give up cinnamic acid to water (Scharling).

When Peru balsam is shaken with strong caustic potash, a solid soap is obtained, a solution of which in water separates into two layers; the upper brownish-yellow layer, the *Perubalsamöl* of Stoltze, containing cinnameïn (and styracin), the lower, the potash-salt of cinnamic acid and resin (Plantamour and others). On distilling the subjacent aqueous liquid, a little more volatile oil is obtained (Scharling). — A mixture of 1 part of Peru balsam with 2 or 3 parts of solution of caustic potash of sp. gr. 1·3, allowed to stand for twenty-four hours and then distilled, yields water, a heavy oil, and a light oil. *a.* The heavy oil, having a sp. gr. of 1·03 at 14°, boils with decomposition at 205°, and does not solidify at − 15°. It has a faint odour, aromatic after long standing. It solidifies in contact with bisulphide of carbon and caustic potash, and according to Scharling, is to be regarded as cinnamate of ethyl, but according to Kraut (*Ann. Pharm.* 107, 208), as benzylic alcohol. — *b.* The light oil, boiling at 180°, smells of anise, tastes sweet and aromatic, and does not solidify at − 15°, It solidifies

with caustic potash and bisulphide of carbon, probably on account of admixture with *a* (Scharling, *Ann. Pharm.* 74, 230). Aqueous alkaline carbonates extract cinnamic acid from Peru balsam.

The balsam mixes with absolute alcohol in all proportions (Pfaff), traces only of the sparingly soluble resin and extractive being deposited. It dissolves in weaker alcohol, with separation of the sparingly soluble resin (Stoltze). Alcoholic potash throws down resinate of potash from the alcoholic solution, whilst cinnamate of potash and cinnameïn precipitable by water remain dissolved (Frémy). Absolute ether takes up cinnamic acid, cinnameïn, and an easily soluble resin (Stoltze). Fusel-oil and valerianic aldehyde dissolve the balsam completely; valerianic acid and valerate of amyl dissolve it with turbidity (Trautwein, *Repert.* 91, 29). Rock-oil extracts impure cinnameïn (Frémy). — The balsam mixes with ⅛th of oil of turpentine; with a larger quantity the mixture separates into two layers (Stoltze). — Oil of almonds dissolves half of the balsam (Pfaff). — Stoltze (*Berl. Jahrb.* 25, 2, 24); Plantamour (*Ann. Pharm.* 27, 329; 30, 341); Frémy (*Ann. Chim. Phys.* 70, 180); Scharling (*Ann. Pharm.* 74, 230; 97, 168). The eight substances obtained by Richter (*J. pr. Chem.* 13, 167) from Peru balsam appear to be either identical with known bodies, or mixtures.

The *resin of Peru balsam* is identical with that of Tolu balsam and benzoïn (xiii, 290) (Frémy). When mixed with pumice-stone and submitted to dry distillation, it yields benzoic acid, water, and an oil consisting of styrol or a similar body (xiii, 2), benzoate of methyl, and carbolic acid (Scharling).

The *sparingly soluble resin* remains behind when the balsam is repeatedly treated with cold alcohol of 75 p. c. It is black-brown, friable, inodorous, and tasteless, neutral, and fusible at a moderate heat, emitting an odour of benzoïn. It dissolves in oil of vitriol with carmine-red colour, and in hot strong caustic potash, from which it is precipitated by acids. Its hot alcoholic solution throws down from neutral acetate of lead, a precipitate soluble in acetic acid. The resin dissolves slightly in hot strong acetic acid, but is insoluble in ether, oil of turpentine, and olive-oil (Stoltze).

The *easily soluble resin* is obtained by neutralising the solution of the balsam in 6 parts of alcohol with carbonate of soda, diluting the solution with water and concentrating, whereupon the liquid separates into three layers. The upper aqueous layer is removed; the lower layers are dissolved in alcohol, the solution is again evaporated, and the residue is dissolved in 12 parts of warm olive-oil, which retains the oil of the balsam in solution, but deposits the resin in flocks on cooling. The flocks are purified by solution in alcohol. Dark-brown, inodorous and tasteless mass, transparent in thin layers, melting below 100°. It dissolves in cold oil of vitriol with dark-violet colour. The alcoholic solution is precipitated of a grey colour by neutral acetate of lead, the precipitate dissolving in acetic acid, and is coloured dark-green by sesquichloride of iron. — The resin dissolves easily in strong acetic acid and in strong alcohol, but not in ether, cold oil of turpentine, or olive acid oil. It is thrown down from the alcoholic solution in grey flocks by gelatin (Stoltze).

The *dried Peru balsam* imported in gourds is reddish-yellow and friable, and contains volatile oil, benzoic acid, and a resin soluble in hot dilute caustic potash, and in alcohol and ether (Trommsdorff, *N. Tr.* 2, 1, 80).

The gum-resin which exudes from the Peru balsam tree contains 77·4 p. c. resin, and 17·1 p. c. gum, besides woody fibre, water, and a little volatile oil. The resin is uncrystallisable, and reddens litmus slightly in alcoholic solution (Attfield, *Pharm. Trans.* (2) 5, 241 ; *Kopp's Jahresber.* 1863, 557).

5. LIQUID STORAX. — The American variety is obtained from *Liquidambar styraciflua*, the Oriental from *Liquidambar Altingia*. — Green-grey, of an agreeable odour and the consistence of honey. Hardens in the air. When distilled, it yields carbonic acid and combustible gas, acid water, benzoic acid (or cinnamic acid ?), a coloured oil which solidifies, and carbon. It gives up benzoic (cinnamic ?) acid to water or milk of lime. — Dissolves in oil of vitriol with brown colour, and is precipitated from the solution in white flocks by water (Dulong). — With excess of nitric acid of sp. gr. 1·2 it yields a large quantity of benzoic acid and a little picric acid (Böttger & Will, *Ann. Pharm.* 58, 274). — It dissolves, with the exception of impurities, in 4 parts of alcohol, forming a brown solution (Bouillon-Lagrange).

Liquid storax is a mixture of styrol (xiii, 1), cinnamic acid (xiii, 268), resins, and styracin (xiii, 286), which occurs in storax partly as acid cinnamate of styracin. *a*. The styrol is obtained by distilling storax with water and carbonate of soda, but in varying quantities, as it becomes converted into a non-volatile body by keeping (Simon). — *b*. The liquid which remains after distilling with water (without carbonate of soda) deposits acid cinnamate of styracin when concentrated. — *c*. The resin remaining on distilling storax with aqueous carbonate of soda, dissolves partly in alcohol and partly in ether ; the alcoholic solution deposits styracin. If the solution be distilled with caustic soda and water before the styracin separates, styracone (xiii, 256) is obtained (Simon).

Storax contains metastyrol (Kovalewsky). When the styrol is removed by distillation with water, the cinnamic acid by treating the residue with caustic soda, and the undissolved portion is then repeatedly washed with alcohol, there remains a solid black resin, which on distillation yields styrol, formed from the metastyrol, and amounting to 1·6 to 2·8 p. c. of the liquid storax (Kovalewsky, *Ann. Pharm.* 120, 66).

Fresh liquid storax is yellow, of the consistence of copaiba balsam at 15°, thicker in the cold, heavier than water, and reddens litmus slightly. It dissolves to the extent of ¾ths in alcohol, leaving crystals, and in all proportions in ether. It contains volatile oil, a waxy substance which passes over with the water and is taken up from the water by ether, benzoic acid, styracin, a soft resin, yellow colouring matter, and a crystalline substance different from styracin. When storax is submitted to prolonged boiling with water and the residual liquid is filtered from resin and evaporated, crystalline granules are deposited, which are to be washed with cold water and triturated with 12 parts of cold water. The undissolved portion, dissolved in boiling water, deposits on cooling nearly colourless crystals, which are rendered quite white by treatment with animal charcoal. They form microscopic four-sided pyramids, neutral, white and shining, having an odour of melilotene, and volatilising on glowing charcoal, therefore probably allied to coumarin (Bonastre, *J. Pharm.* 17, 345 ; *N. Tr.* 24, 2, 236).

6. SOLID STORAX. — From *Styrax officinalis*. Occurs either in yellow translucent granules of the size of peas and the hardness of wax (*Storax in granis*), or in brown, yellow, or white coherent pieces, sticky when warmed (*Storax in massis*); or in brown cakes made up of storax, sawdust, and other impurities (*Scobs storacina, Storax cala-mita*). Has a very agreeable odour and a burning taste. When distilled with water, it gives off its oil only after all the water has passed over. The oil is at first limpid and afterwards buttery; it is empyreumatic and contains benzoic acid (Neumann). It forms with oil of vitriol a red solution from which water throws down red flocks (Dulong). It is soluble in alcohol. — Contains styracin, uncrystal-lisable soft resin, colouring matter, and benzoic acid, the last of which may be extracted by boiling with lime, but not by boiling water: neither does the aqueous decoction redden litmus (Lepage, *J. Chim. méd.* 18, 727).

The solid *Storax from Bogota* contains easily soluble resin, benzoic acid, bitter extractive, and 40 p. c. of woody fibre (Bonastre, *J. Pharm.* 16, 88; *N. Tr.* 21, 2, 242).

The *Storax calamita* of 1785 was very light, crumbly between the fingers, had an odour of benzoïn, and appeared to consist almost entirely of needles of benzoic acid and yellow pieces of resin. When heated, it yields a sublimate of benzoic acid, and when distilled with water, a milky distillate from which ether extracts a stearoptene. The residual water deposits crystals on evaporation, and leaves a dark-yellow gum. The undissolved portion forms with alcohol a brown-red tincture containing benzoic acid (cinnamic acid?) and resins, while woody fibre remains undissolved. — The same constituents, together with ammonia and caoutchouc, are present in the reddish heavy, and the brown granular *Storax calamita* of commerce, and are therefore not to be regarded as artificial products (Reinsch, *Repert.* 63, 289).

7. TOLU BALSAM. — From *Myrospermum toluiferum* or *frutescens*. Yellowish to pale red-brown, and of the consistence of turpentine in the fresh state (*white Tolu balsam*). Becomes hard and reddish-brown on keeping (*black Tolu balsam*), and dries up in the air to a brittle solid resinous mass (*dry Tolu balsam*). — The following varie-ties are to be distinguished: *a.* The ordinary balsam from Carthagena; reddish-yellow, not quite transparent, granular, or crystalline, brittle in the cold, softening in the mouth. — *b.* The turpentine-like balsam from Brazil, which becomes harder than the preceding when exposed to the air. It yields cinnamic acid to warm water (St. Martin, *Pharm. Viertelj.* 14, 110). Tolu balsam from Santa Fe de Bogota is very soft, contains a little benzoic acid, and yields by distillation a fluid balsamic oil, in part lighter than water (Bonastre, *J. Pharm.* 19, 676; *Ann. Pharm.* 10, 128).

Tolu balsam has an agreeable odour and a warm, sweetish, biting taste. — When exposed to the air on a plate, it gradually dries, becoming crystalline and richer in acid (Guibourt; Scharling). — It dissolves in oil of vitriol with red colour, and in nitric acid with evolu-tion of hydrocyanic acid, and when distilled with the latter acid yields benzoic acid, together with Hatchett's artificial tannin. — When boiled or digested with aqueous carbonate of soda, it forms a brittle mass, which turns red in the air. — It does not dissolve com-

pletely in caustic potash of sp. gr. 1·06, even when warmed, but is soluble in a solution of sp. gr. 1·17, without separation of oil (or cinnameïn). Caustic potash of sp. gr. 1·27 forms with it a clear solution, which afterwards solidifies (Scharling). — It dissolves in 6 parts of alcohol (Planche), less easily in ether and volatile oils, not completely in fat oils.

Tolu balsam is a mixture of a little volatile oil, free acid, and resin. *a.* The volatile oil obtained by distillation with water contains tolene (xiv. 312), benzoic acid, and cinnameïn (xiii, 28), also a body boiling at 180°, and containing 84·9 p. c. C., 11·83 H., and 3·27 O., probably a hydrate of tolene (Deville). By dissolving the balsam in dilute caustic potash, Frémy obtained also cinnameïn, which separated in the form of an oil; Scharling, however, denies its existence in Tolu balsam. — *b.* The acid of the balsam is cinnamic acid (Frémy), a mixture of cinnamic and benzoic acids (Deville); the benzoic acid is not formed, as Kopp imagines, by the action of alkalis on the resins, but may be extracted by carbonate of soda or distilled off with vapour of water at 170° (Scharling).

*c.* On the *resins of Tolu balsam* see xiii, 290. Kopp's alpha-resin appears not to be a peculiar body, but if the residue which is left on distilling Tolu balsam in a current of superheated steam be treated with weak and with strong alcohol, there remains a portion nearly insoluble in alcohol, ether, bisulphide of carbon, and oil of turpentine, but soluble for the most part in caustic potash, and precipitable by hydrochloric acid from the alkaline solution in the form of a jelly having the same composition as the beta-resin (xiii, 291) (Scharling).

When Tolu balsam, freed from volatile oil and dehydrated by heat, is subjected to dry distillation, a colourless viscid distillate which afterwards crystallises is obtained, containing toluene (xii, 226), benzoate of methyl [according to Scharling; but according to Deville, benzoate of ethyl (xii, 60)], benzoic acid, and a little cinnamic acid: on continuing the distillation, a violent frothing takes place for some time, after which the mass boils quietly, yielding a distillate of water and a heavy, limpid oil, carbonic oxide and carbonic acid being evolved, whilst charcoal remains behind (Deville). The balsam freed from acid by carbonate of soda dissolves in boiling strong caustic potash, forming a brown liquid which solidifies on cooling in a granular mass, completely soluble in water, and yielding toluol on distillation (Kopp). — When the resin of Tolu balsam is distilled with coarsely powdered pumice, 31 p. c. of an acid brown oil is obtained, consisting of a mixture of methylic benzoate, toluol, and carbolic acid (Scharling). — Frémy (*Ann. Chim. Phys.* 70, 201); H. Deville (*N. Ann. Chim. Phys.* 3, 151); E. Kopp (*Compt. Chim.* 1849, 145); Scharling (*Ann. Pharm.* 97, 88).

8. MECCA BALSAM. Source, xiv, 383. — Limpid, pale-yellow, of sp. gr. 0·95. Smells fragrant, or, after standing for some time in the air, like turpentine; tastes bitter and warm. When exposed to the air, it rapidly becomes thick, viscid, and specifically heavier. It dissolves easily in alcohol and ether.

Mecca balsam distilled with water yields volatile oil (xiv, 383), a very bitter aqueous decoction, a resin soluble in cold alcohol, and a second resin insoluble in that liquid. Much of the balsam also contains gum. — The *soluble resin* is soft, of acid reaction, insoluble in aqueous ammonia, and soluble in small quantity only in boiling nitric

acid : it does not combine completely with an equal quantity of caustic potash and water. — The *insoluble resin* is moderately hard, of a whitish-grey colour, inodorous and tasteless, and softens with difficulty when warmed. It dissolves very slightly in boiling alcohol, from which it is thrown down in white flocks on cooling, but is easily soluble in ether (Bonastre, *J. Pharm.* 18, 98 ; *Ann. Pharm.* 3, 147). Trommsdorff (*N. Tr.* 16, 1, 76), by boiling the balsam first with water and then with absolute alcohol, obtained a yellowish-brown, soft, viscid residue, without smell or taste, which dried up gradually when warmed, melted at 100° to 110°, and at a higher temperature evolved acid and aromatic vapours, and burnt with a bright flame. It swelled up in cold strong nitric acid and also in the hot dilute acid, was insoluble in ammonia and in boiling caustic potash, but easily soluble in warm volatile and fat oils, and became suspended in boiling absolute alcohol without dissolving. — The portion of Mecca balsam taken up by absolute alcohol remains on evaporation as a friable, transparent, honey-yellow mass of sp. gr. 1·33, which softens at 44° and becomes limpid at 92°. It yields by distillation a yellow oil, a little water, and a little combustible gas, whilst a dark brittle resin remains behind. It forms with nitric acid of sp. gr. 1·55, oxalic acid and yellow products, and with cold oil of vitriol, a brown-red solution. It is insoluble in ammonia and caustic potash, slightly soluble in absolute alcohol and cold ether, but more easily soluble in these liquids when warm, and in warm volatile and fatty oils (Trommsdorff ; Vauquelin, *Ann. Chim.* 69, 221).

Mecca balsam from an Egyptian tomb was solid, fusible, and contained an admixture of crystals. When distilled with water, it yielded acetic acid, but no volatile oil or benzoic acid. The balsam exhausted with boiling water is decomposible by alcohol into two resins : the crystals also dissolve in alcohol. The crystals are cauliflower-like, slightly acid, nearly tasteless, fusible only above 90°, and not susceptible of sublimation (Bonastre, *J. Pharm.* 18, 336).

*Lançon* or *Landsome*, a balsam obtained from the Philippines, separates, on standing, into an upper yellow and a lower turbid layer, which are not miscible. It is less fluid than balsam of copaiba, more fluid than Venice turpentine, and dissolves in cold alcohol with the exception of a white residue. — When distilled with water, it yields 20 p. c. of volatile oil (xiv, 373) and a soft residue, from which cold alcohol of 36° takes up a resin, the rest remaining undissolved. — The soluble resin is transparent, difficultly saponifiable, and slowly decomposed by nitric acid, which colours it reddish-violet. — The insoluble resin, obtained by dissolving in alcohol and evaporating the solution, is amorphous, inodorous, tasteless, and insoluble in alkalis. When warmed with nitric acid it assumes a faint rose-red colour, arising from the presence of volatile oil (Bonastre, *J. Pharm.* 15, 662 ; *N. Tr.* 21, 2, 215).

The balsam of *Hedwigia balsamifera* or *Bursera balsamifera* exudes from the inner bark of the tree. The balsam 30 years old is dark-red, soft, viscid, and sticks to the fingers : it has an odour of turpentine and a burning bitter taste. It contains a soft resin easily soluble in alcohol, a hard resin insoluble in cold alcohol, volatile oil (xiv, 371), bitter principle, sugar, lime, and potash-salts (Bonastre, *J. Pharm.* 12, 485 ; *Repert.* 26, 134).

Concerning the balsam of *Terminalia vernix* (*Vernis de la Chine*), which contains benzoic acid, see Macaire-Princep (*J. Pharm.* 15, 525 ; *N. Tr.* 21, 1, 107).

## Stearoptene from Oil of Cassia.

ROCHLEDER & SCHWARZ. *Wien. Akad. Ber.* 5, 77; *J. pr. Chem.* 51, 432; *Kopp's Jahresber.* 1850, 509. — *Wien. Akad. Ber.* 12, 192; *J. pr. Chem.* 63, 129; *Pharm. Centr.* 1854, 701; *Kopp's Jahresber.* 1854, 590.

The partly colourless, partly yellow crystalline masses deposited from oil of cinnamon (xiii, 258) are obtained by recrystallisation from a small quantity of alcohol, in colourless, inodorous, shining, brittle prisms, which melt to a colourless, highly refractive oil when heated, volatilise at a higher temperature, and solidify to a yellow lamellar mass on cooling.

The crystals contain, on the average, 75·20 p. c. C., 6·83 H., and 17·97 O., from which numbers Rochleder deduced the formula $C^{28}H^{15}O^5$, and afterwards $C^{56}H^{29}O^{10}$. — They are converted by nitric acid into a nitrogenous acid exhibiting the behaviour of nitrobenzoic acid, but containing 45·48 p. c. C., and 3·95 H. (probably $C^{14}H^7XO^6$). — The stearoptene forms with ammonia a nitrogenous product, and with caustic potash, when distilled therewith, a volatile oil containing 69·63 p. c. C., 6·18 H., and 24·29 O., together with a little brown resin.

When the stearoptene is boiled with aqueous bisulphite of soda for five minutes, it melts to an oil, colours the solution yellow, and dissolves on cooling with the exception of admixed resin. The filtrate deposits crystals of benzhydrolic acid, after the removal of which, the filtrate yields benzhydrol; (*a*) on boiling the solution, as a floating oil which afterwards solidifies; (*b*) on addition of dilute sulphuric acid.

*Benzhydrolic acid,* purified by dissolving it in lime-water and precipitating with hydrochloric acid, forms colourless or yellowish crystalline flocks which lose water in a vacuum. — Benzhydrol (differing from Linnemann's benzhydrol, a product obtained by treating benzophenone with sodium-amalgam), has the composition *a* and *b* [when obtained according to *a* and *b* (above)]: when melted for several hours at 110° and then cooled, it solidifies to a crystalline mass *c*. It assumes a yellow to black colour in the air.

*Analyses by Rochleder & Schwarz.*

| | Benzhydrolic acid. | | | | Benzhydrol. | | |
|---|---|---|---|---|---|---|---|
| | Air-dried (*a*). | In vacuo (*b*). | *a.* | | *b.* | | *c.* |
| C | 71·28 | 72·84 | 74·63 | | 75·66 | | 72·57 |
| H | 6·23 | 6·25 | 6·45 | | 6·45 | | 6·34 |
| O | 22·49 | 20·91 | 18·92 | | 17·89 | | 21·09 |
| | 100·00 | 100·00 | 100·00 | | 100·00 | | 100·00 |

Rochleder gives the following formulæ: for benzhydrolic acid *a* and benzhydrol *c*, $C^{42}H^{21}O^9$; for the acid *b*, $C^{42}H^{22}O^{10}$; for benzhydrol *a* and *b*, $C^{42}H^{21}O^8$ and $C^{28}H^{14}O^5$.

When a solution of benzhydrolic acid in lime-water is neutralised with nitric acid and precipitated with nitrate of silver, white flocks of a *silver-salt* are obtained, containing 55·14 p. c. C., 4·58 H., 17·50 O., and 22·78 AgO. — Benzhydrol forms also with bisulphite of soda a compound containing 20·13 p. c. soda and 32·42 p. c. carbon.

### B. *Resins free from Benzoic Acid.*

**1. ALOUCHI RESIN.** From a tree growing in Madagascar. Dirty-white externally, blackish and marbled within, opaque, solid, and friable. Has a strongly aromatic odour, resembling pepper, and a bitter taste. Contains volatile oil, a resin easily soluble in alcohol, a second resin sparingly soluble in alcohol, free ¡acid, ammonia-salt, bitter extractive and impurities.

The *sparingly soluble resin* occurs to the extent of 20·45 p. c. in the crude resin. To obtain it the resin is washed repeatedly with cold alcohol, the residue is boiled with alcohol, and the solution filtered, whereupon the sparingly soluble resin separates from the filtrate in flocks. — It forms very fine, light, pearly, radiated groups of needles, harsh to the touch and phosphorescent. It melts when heated and volatilises with resinous odour, subliming in small laminæ : if the heat has been cautiously applied, the residue is not coloured. It is insoluble in boiling caustic soda, slightly soluble in boiling alcohol, and more easily in ether (Bonastre, *J. Pharm.* 9, 180 ; 10, 1). See also Vauquelin (*Ann. Chim.* 72, 299).

**2. GUM AMMONIACUM.** — From *Dorema armeniacum.* Yellowish-white, translucent pieces, friable in the cold, having a conchoïdal fracture and a fatty lustre on the fractured surface. Has a repulsive odour, and a slightly bitter and acrid taste. Its alcoholic solution reddens litmus. It contains a brittle resin soluble in alkalis and alcohol, also gum, bassorin, and a transparent light oil, besides woody fibre and sand. It forms a milk with water. When submitted to dry distillation, it does not melt, and yields no umbelliferone (Sommer), but according to Braconnot (*Ann. Chim.* 68, 69) ammoniacal products. — With nitric acid of sp. gr. 1·2, it forms styphnic acid (xi, 228), but no other acid (Böttger & Will). Nitric acid of sp. gr. 1·35 dissolves it after boiling for a short time : the solution deposits a soft yellow resin when mixed with water, and more when concentrated and again diluted, whilst camphretic acid $C^{40}H^{14}O^{14}$ remains in solution (Schwanert, *Ann. Pharm.* 128, 123). — Gum ammoniacum melted with caustic potash yields protocatechuic acid and resorcin (xvii, 240) (Hlasiwetz & Barth).

Commercial gum ammoniacum increases but little in volume when digested with cold alcohol of sp. gr. 0·83, but yields a pale-yellow solution, which leaves on evaporation a clear, nearly colourless resin, having the odour of the gum, and assuming a yellow colour, with partial loss of odour at 100°. It is easily fusible, precipitable from the alcoholic solution by neutral acetate of lead as a white precipitate, and contains, on the average, 70·95 p. c. C., 7·59 H., and 21·46 O., corresponding to the formula, $C^{40}H^{25}O^{9}$. When heated to 131° it becomes thicker and darker, without frothing or giving off visible vapours, and then contains about 1 p. c. more of carbon (Johnston, *Phil. Trans.* 1840, 350.)

**3. GUM ANIME.** That obtained from the locust-tree *Hymenea Courbaril* is yellow, translucent, of sp. gr. 1·028 to 1·03, and softens in the mouth. It tastes like mastic, and emits a peculiar odour when warmed. Its alcoholic solution reddens litmus. — It does not yield umbelliferone by dry distillation (Sommer). Contains volatile oil (xiv, 358), an easily soluble and a difficultly soluble resin, the latter of which remains behind

on treating the gum with alcohol. It dissolves in warm aqueous ammonia (Paoli, *Brugn. Giorn.* 16, 187 and 325 ; *N. Tr.* 9, 1, 40 and 61). Cold alcohol takes up from gum anime, oil and an amorphous resin, probably pinic acid : the residue, dissolved in boiling alcohol, deposits on cooling, very delicate needles in the form of light flocks, containing 83·02 p. c. C., 11·50 H., and 5·48 O., corresponding to the formula $C^{40}H^{38}O$ (Laurent, *Ann. Chim .Phys.* 66, 314). Gum anime dissolves in benzene (Mansfield) and partially in creosote (Reichenbach). Concerning other varieties of anime, see Paoli, Manzini (*J. Pharm.* 27, 752), Hancock (*Ed. N. J. of Sc.* 1, 240), Guibourt (*Rév. scient.* 16, 177).

## 4. Resin from Arbol-a-Brea.

MAUJEAN. *J. Pharm.* 9, 45.
BONASTRE. *J. Pharm.* 10, 199.
DUMAS. *J. Chim. méd.* 21, 309 ; *J. Pharm.* 21, 193 ; *Ann. Pharm.* 15, 160 ; *J. pr. Chem.* 4, 436.
BAUP. *N. J. Pharm.* 20, 321 ; *Ann. Pharm.* 80, 312 ; *J. pr. Chem.* 55, 83.

Obtained from incisions in a tree [probably *Canarium album* (Baup)] growing in Manilla. — Soft, greyish-green, sticky resin, having a powerful odour of turpentine, cubebs, and fennel, and behaving towards alcohol and volatile and fatty oils in the same manner as elemi (Maujean).

According to Bonastre, it contains a light greenish-yellow volatile oil, an easily soluble and a difficultly soluble resin, the latter of which forms radiated groups of white shining crystals, containing, according to Dumas, 85·3 p. c. C., 11·7 H., and 3·0 O.

On treating the resin with cold alcohol of 85 p. c. volatile oil, breïn, bryoïdin, and breïdin are dissolved, whilst amyrin remains behind. The solution is evaporated, whereby the volatile oil is driven off, and the residue is treated with water and with alcohol of 50 p. c. in succession, which take up the bryoïdin and breïdin, but leave the breïn undissolved. On evaporating the mixed solutions, the bryoïdin is obtained in drops, which afterwards become solid, whilst the breïdin remains in the mother-liquor.

a. *Amyrin.* — Purified by solution in boiling alcohol of 90 to 95 p. c. and recrystallisation. Identical with Bonastre's difficultly soluble resin and with the amyrin of elemi resin. — Silky fibres, melting at 174°, soluble in ether.

b. *Breïn.* — This body is purified by dissolving it in 85 p. c. alcohol and evaporating the solution slowly, whereupon it crystallises in transparent rhombic prisms of 110 and 70°, having two bevelling faces inclined to one another at an angle of 80°. It melts at 187°, is insoluble in water, but soluble in 70 parts of 85 p. c. alcohol at 20°, and easily in ether.

c. *Bryoïdin.* — Crystallises from hot water, and likewise from aqueous alkalis or dilute acetic acid, in white silky fibres having a biting, slightly bitter taste. It melts at 135°, and solidifies suddenly, on

cooling, to a nodular, fibrous mass. Volatilises below its melting-point without leaving a residue. Neutral. — Dissolves in 350 parts of water at 10°, and in a smaller quantity of hot water: the solutions are precipitated by neutral acetate of lead and more abundantly by the basic acetic. Dissolves easily in alcohol, ether, oil of turpentine, and fat oils.

d. *Breïdin.* — Transparent rhombic prisms of 102° and 78°, with four-sided summits. Becomes opaque when warmed, melts a little above 100°, and sublimes without residue. Dissolves in 260 parts of water at 10°, and more easily in hot water. Soluble in alcohol, and less freely in ether (Baup).


## 5. Asafœtida.

TROMMSDORFF. *N. Tr.* 1, 2, 137.
PELLETIER. *Bull. Pharm.* 3, 556.
BRANDES. *Repert.* 7, 1.
ANGELINI. *Brugn. Gion.* 19, 174; *Kastn. Arch.* 9, 101.
ZEISE. *Schw.* 46, 324, — REIGEL, *Jahrb. pr. Pharm.* 4, 348.
REINSCH. *Jahrb. pr. Pharm.* 12, 362.
JOHNSTON. *Phil. Trans.* 1840, 354.
STENHOUSE. *Phil. Mag.* 20, 575; *Mem. Chem. Soc.* 1, 43; *J. pr. Chem.* 27, 255; *Ann. Pharm.* 44, 309.
HLASIWETZ. *Ann. Pharm.* 71, 23.

*Stinkasant. Devil's dung. Teufelsdreck.* — From *Ferula Asafœtida* (Handbuch, viii [2], 45) and other species. — White masses turning rose-red, violet, and brown in the air; friable in the cold, tough when warmed, having a fetid odour of garlic, and an acrid bitter taste.

Asafœtida contains volatile oil, gum (according to Brandes and Pelletier, also bassorin), a resin soluble in alcohol and ether, and a second resin insoluble in ether (Brandes). Asafœtida frequently exhibits needles of gypsum when broken (Riegel). Its alcoholic extract submitted to dry distillation yields a colourless oil, then acid water, a green, and lastly, a blue oil having an odour of creosote, together with umbelliferone. When asafœtida is digested with oil of vitriol of sp. gr. 1·75, the resulting black-red pulp boiled with water, and the extract neutralised with carbonate of lime, the filtrate likewise contains umbelliferone (Sommer). — With nitric acid of sp. gr. 1·2 asafœtida forms styphnic acid (xi, 228) (Böttger & Will). — Asafœtida treated with caustic potash and then with acid, evolves hydrosulphuric acid; when treated with nitric acid, it also yields sulphuric acid, and the sulphuretted oil contained in it (Zeise). — When distilled with an equal quantity of hydrate of lime and a little water, it yields a colourless oil, having a burning taste and an odour different from that of asafœtida. The residue contains resins in combination with lime (Reinsch). — When asafœtida is melted with caustic potash, an acid is formed resembling that produced by the similar treatment of guaiacum (Hlasiwetz & Barth).

Commercial asafœtida increases but little in bulk when digested with cold alcohol of sp. gr. 0·83: the pale-yellow solution formed

leaves on evaporation a pale-yellow resin, which quickly assumes a purple colour in sunshine. It dissolves easily in cold alcohol and ether, and produces with alcoholic neutral acetate of lead, a dense white precipitate, and according to Johnston, does not yield sulphuric acid when decomposed by nitric acid, or when deflagrated with chlorate of potash and chloride of sodium. When heated above 100° it froths up for a while, giving off a powerful odour of garlic, after which it flows tranquilly, and after cooling is darker, less odorous, and brittle, but still perfectly soluble in alcohol. It contains, at 100°, on the average, 68·65 p. c. C., 7·56 H., and 23·79 O.; and after melting till it becomes inodorous, 70·18 p. c. C., 7·63 H., and 22·21 O. — When the alcoholic tincture of asafœtida is poured into a large quantity of boiling water and boiled (whereby volatile oil is driven off), and the yellow powder which is deposited on cooling is again dissolved in alcohol, evaporated, and dried at 100°, the residue contains 70·44 p. c. C., 7·68 H., and 21·88 O. (Johnston). Johnston appears to have overlooked the sulphur here (Kr.).

When an alcoholic tincture of asafœtida is freed from volatile oil by distillation, and the residue is precipitated by water, the *resin* is obtained as a yellowish-white, nearly inodorous precipitate, which rapidly turns rose-red in the air. It dissolves in oil of vitriol with green colour, and is precipitated from the solution in rose-red flocks by water. On dry distillation, the resin first froths up and gives off water, hydrosulphuric acid, and asafœtida oil, and then boils quietly, yielding aromatic oils of a green, blue, violet, and red colour. These oils, when shaken with caustic potash, colour it yellow, and become turbid. The violet portion of the oils becomes deep-red on exposure to the air. The yellow alkaline solution distilled with sulphuric acid evolves hydrosulphuric acid, and yields an acid distillate, which is turbid from the presence of heavy oily drops: the distillate contains formic acid and a trace of acetic acid, and after neutralisation with carbonate of soda, reduces nitrate of silver (Hlasiwetz).

The *volatile oil of asafœtida*, when gradually heated to redness with potassium, yields a mixture of carbon and sulphide of potassium (Zeise). It is free from nitrogen (Will; Stenhouse). When obtained by distilling the powdered resin with powdered glass and water, it is of a yellowish colour, of sp. gr. 0·943 at 15·5°, tastes mild, and afterwards acrid, and resinises in the air. After being twice rectified, it begins to boil at 163°, the boiling-point rising to 188°. The oil dissolves iodine easily, without explosion. It does not combine with ammonia, and is but little affected by aqueous or alcoholic potash. Nitric acid resinises it, with abundant evolution of nitric oxide and formation of sulphuric acid. Oil of vitriol turns it red, and carbonises it when heated. The oil precipitates salts of lead, mercurous oxide, and silver black, solution of sublimate white, and when dropped into melted caustic potash, gives up a portion, but not the whole, of its sulphur (Stenhouse).

Analyses by Stenhouse.

| | Oil at 163°. | | at 172°. Distillate. | | at 188°. |
|---|---|---|---|---|---|
| C ............... | 65·97 | ............ | 62·57 | ............ | 58·23 |
| H... ............ | 9·73 | ............ | 9·25 | ............ | 9·10 |
| S ....... ....... | 22·74 | ....... ... | 20·06 | ............ | 16·31 |
| O ................. | 1·56 | ............ | 8·12 | ............ | 16·36 |
| | 100·00 | ............ | 100·00 | ............ | 100·00 |

When asafœtida is distilled with water in a flask placed in a bath of chloride of sodium, volatile oil amounting to $\frac{1}{32}$nd of the asafœtida is obtained, a part of which is dissolved, together with valerianic and propionic acids, in the water which passes over at the same time. If a copper vessel be employed, the sides become coated with sulphide of copper. — The oil is pale-yellow, limpid, and neutral, has a penetrating odour of asafœtida, and a mild, afterwards harsh taste. It does not redden the skin, does not solidify in a freezing mixture, and boils at 130° to 140°, with evolution of hydrosulphuric acid. It is a mixture, in varying proportions, of two sulphuretted oils free from oxygen, probably $C^{12}H^{11}S$ and $C^{12}H^{10}S^2$ (Hlasiwetz).

<div style="text-align:center"><em>Calculation.</em></div>

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 12 C | ............ | 72 | ........ | 72·73 | 12 C ............. | 72 | ........ 63·16 |
| 11 H | ............ | 11 | ........ | 11·11 | 10 H ............. | 10 | ........ 8·77 |
| S | ............ | 16 | ........ | 16·16 | 2 S ............. | 32 | ........ 28·07 |
| $C^{12}H^{11}S$ | ........ | 99 | ........ | 100·00 | $C^{12}H^{10}S^2$........ | 114 | ........ 100·00 |

<div style="text-align:center"><em>Analyses.</em></div>

| | a. | | b. | | c. | | d. |
|---|---|---|---|---|---|---|---|
| C | 67·13 | ........ | 65·24 | ........ | 65·46 | ........ | 69·27 |
| H | 10·48 | ........ | 9·55 | ........ | 9·09 | ........ | 10·42 |
| S | 22·37 | ........ | 25·37 | ........ | 25·43 | ........ | 20·17 |
| | 99·98 | ........ | 100·16 | ........ | 99·98 | ........ | 99·86 |

*a* and *b* were distilled from copper vessels; *c* from a glass flask; *d* was evaporated at 120—130°, without boiling the liquid. Gmelin regarded as probable the formulæ $C^{10}H^8S^2$ (60 p. c. C., 8 H., and 32 S.) and $C^{10}H^9S$ (70·59 p. c. C., 10·59 H., and 18·82 S.)

The oil evolves hydrosulphuric acid on standing, and when kept in vessels containing air, acquires a different odour, and becomes slightly acid. — Strong *nitric acid* acts violently upon it, even causing inflammation: when cautiously oxidised, the oil yields acetic, propionic, and a large quantity of oxalic acid. — When heated with *chromic acid*, it yields acetopropionic and probably also formic acid.

Many *desulphuretting agents*, when brought in contact with asafœtida oil, form metallic sulphides, and separate an oil which is richer in sulphur than the original oil (probably $C^{48}H^{44}S^9$), volatile acids being produced at the same time: *a.* On shaking the crude oil with caustic potash saturated with oxide of lead so long as sulphide of lead is formed, rectifying the remaining portion, and drying it over chloride of calcium, the product is but slightly coloured, and has an odour of lavender and rosemary. — *b.* A similar oil is obtained by digesting the crude oil with hydrated oxide of lead. — *c.* On passing sulphurous acid gas for some time through the crude oil mixed with water, a dingy-coloured resin is deposited: the decanted oil, when washed with carbonate of soda and water, and rectified, resembles *a* and *b.* — *d.* By passing the vapour of the crude oil over heated soda-lime, or by dropping the oil on soda-lime at 200°, $\frac{1}{16}$th of the oil distils as a clear liquid, which has an odour of lavender, and gives up a little hydrosulphuric acid to caustic potash. In this reaction, propio-valerianic and acetic acids are produced. — *e.* Solution of caustic soda and hydrate of soda heated to 120°, produce formic acid and a little acetic acid, but no propionic or valerianic acid. With hydrate of soda the oil swells

up to a green-brown, thick mass, which dissolves in water when heated therewith for an hour and a half, giving off an odour of lavender. — *f*. With excess of silver-oxide, a black mixture containing sulphide of silver and metallic silver is obtained, from which an oil having the composition of the oil employed is expelled by heat, together with a little hydrosulphuric acid. Oxide of silver, therefore, oxidises one part of the oil, leaving the other part unaltered.

| *a.-d.* according to Hlasiwetz. | | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* |
|---|---|---|---|---|---|---|---|
| 48 C ....... | 288 .... | 60·50 .... | 60·16 .... | 60·76 .... | 60·49 .... | 60·52 .... | 76·89 .... | 65·66 |
| 44 H ........ | 44 .... | 9·25 .... | 9·43 .... | 9·52 .... | 9·36 .... | 10·13 .... | 11·36 .... | 10·14 |
| 9 S ........ | 144 .... | 30·25 .... | 29·85 .... | | 31·08 .... | 29·77 .... | 11·62 .... | 24·81 |
| $C^{48}H^{44}S^9$.... | 476 .... | 100·00 .... | 99·44 .... | | 100·93 .... | 100·42 .... | 99·87 .... | 100·61 |

The oil $C^{10}H^9S$, therefore, is oxidised, whilst $C^{10}H^8S^2$ remains (Gmelin).

Asafœtida oil, treated with *hydrochloric acid gas*, acquires a red, violet, and black colour, and becomes thick. — *Chlorine* acts in a similar manner, hydrochloric acid and chloride of sulphur being evolved, and a black stinking tar remaining. — With *monosulphide of potassium* at 150°, and with the pentasulphide at 185°, a turbulent evolution of hydrosulphuric acid takes place, the oil becoming darker and passing over undecomposed in very small quantity only. — Potassium produces a copious evolution of gas, becoming covered with sulphide, and decomposes the whole of the oil, with the exception of a small portion still containing sulphur. The sulphide of potassium produced, when treated with an acid, evolves a powerful odour of cinnamon after the greater part of the hydrosulphuric acid is given off. Oil of asafœtida, heated in *ammonia-gas*, yields an abundant sublimate of sulphide of ammonium. — The oil is scarcely altered by *sulphocyanide of potassium* in a sealed tube at 160—200°, and does not form oil of mustard.

Oil of asafœtida is moderately soluble in *water*.

*Mercury-compound.* — The white flocks which are produced on mixing strong alcoholic solutions of the crude oil and of mercuric chloride acquire a grey colour when allowed to stand under the liquid, from admixture with sulphide of mercury. If it be collected at once and boiled with alcohol, a small portion dissolves and crystallises from the filtrate in delicate white needles, the greater part remaining behind as a grey-white powder, which turns black with caustic potash, and contains only 1·72 p. c. of carbon, but behaves towards sulphocyanide of potassium in the same manner as the crystals. — After drying, the crystals are insoluble in water, very slightly soluble in alcohol, and soluble in nitric acid only after addition of a drop of hydrochloric acid. They turn yellow with caustic potash, and give off an odour of oil of mustard when triturated with sulphocyanide of potassium : when heated with the latter reagent, they yield drops of oil of mustard, which forms, with ammonia, crystals of thiosinnamine, a large quantity of the oil, however, remaining fluid. — The crystals contain 14·03 p. c. C., 2·39 H., 61·19 Hg., 10·93 Cl., besides sulphur, and according to Hlasiwetz, are represented by the formula $C^{12}H^{10}S^2,5HgS$ + $C^{12}H^{10}S^2,HgCl$.

*Platinum-compound.* — *a.* Alcoholic solution of bichloride of pla-

tinum mixed with alcoholic oil of asafœtida throws down, first a pale-yellow precipitate, which increases in bulk and becomes darker and at last red-brown, from admixture of sulphide of platinum. — b. On heating the mixed solutions containing excess of platinum, to boiling, and filtering, there remains on the filter a dark-brown powder (b) : the filtrate deposits on cooling pale-yellow flocks (c), which are insoluble in water, dilute acids, and alcohol.

|  | Calculation according to Gmelin. |  |  |  | Hlasiwetz. a. |  | b. |  | c. |
|---|---|---|---|---|---|---|---|---|---|
| 20 C | 120 | .... | 25·66 | .... | 18·83 | .... | 17·31 | .... | 24·90 |
| 18 H | 18 | .... | 3·85 | .... | 3·19 | .... | 3·03 | .... | 3·87 |
| 2 Pt | 198 | .... | 42·35 | .... | 47·48 | .... | 52·11 | .... | 44·17 |
| 6 S | 96 | .... | 20·54 | .... | 17·53 | .... | 18·87 | .... | 20·26 |
| Cl | 35·5 | .... | 7·60 | .... | 13·54 |  |  |  |  |

$C^{20}H^{18}S^4,PtS^2 + PtCl$.... 467·5 .... 100·00 100·57

No calculation is possible for a and b, on account of the admixture of sulphide of platinum.

Oil of asafœtida dissolves very easily in *alcohol* and *ether* (Hlasiwetz).

6. BDELLIUM. — *From various species of Balsamodendron* (Perottet, *N. J. Pharm.* 1, 408 ; Richard, *Ann. Pharm.* 7, 321 ; *Handbuch,* viii [2], 19). Reddish-brown and yellow, flexible, softening between the teeth. Has a bitter taste, and an odour of myrrh. Sticks to the fingers (Bley & Diesel). Contains 59 p. c. of resin, gum, bassorin, and heavy volatile oil. When subjected to dry distillation, it yields a stinking oil and acetate of ammonia (Pelletier, *Bull. Pharm.* 4, 52). The aqueous extract does not precipitate lead-salts. — Bdellium turns soft, white, and opaque in nitric acid (Bley & Diesel, *N. Br. Arch.* 43, 304).

The resin of bdellium is transparent, and melts at 55° to 60°. It becomes white and opaque by boiling with water (Pelletier).

On digesting bdellium with cold alcohol of sp. gr. 0·83, evaporating the pale-yellow tincture, and boiling the residue repeatedly with water (which thereby acquires a yellowish colour), and drying it at 82° to 93°, it appears as a yellow transparent mass, softening at 100°, with faint resinous odour. It contains 75·50 p. c. C., 9·87 H., and 13·80 to 14·63 O. (Johnston, *Phil. Trans.* 1840, 368).

# 7. Betulin or Birch-camphor.

LOWITZ. *Crell. Ann.* 1788, 2, 312.
JOHN. *Dessen Chem. Schriften.* 5, 93.
OWEN MASON. *Sill. Amer. J.* 20, 282 ; *Berz. Jahresber.* 12, 242.
HÜNEFELD. *J. pr. Chem.* 7, 53.
HESS. *Ann. Pharm.* 29, 135 ; *J. pr. Chem.* 16, 161 ; *Pogg.* 46, 312.

Occurs in the outer bark of the birch tree, from which it is expelled in woolly flocks when birch-wood is heated over a clear fire till the bark becomes dry and brown. John obtained it also in small quantity by distilling the outer bark with dilute sulphuric acid.

*Preparation.* Dried and comminuted birch-bark is exhausted with boiling water. It is then dried, and the betulin is extracted with boiling alcohol. The tincture on cooling deposits the betulin, which is collected, pressed, allowed to dry perfectly, and crystallised repeatedly from ether (Hess). Mason adopts a similar process. Hünefeld boils the bark with the strongest alcohol, distils the alcohol completely from the tincture, collects the residual yellowish-white betulin on a strainer, then presses, dries, and dissolves it in ether-alcohol. He then adds to the solution, first levigated neutral acetate of lead, which produces a yellowish precipitate, then animal charcoal; digests; filters the liquid; and throws down the lead from the filtrate by means of strong aqueous carbonate of ammonia. The liquid, again filtered and mixed with water, deposits the betulin, which is purified from small quantities of resin by again precipitating its solution in ether-alcohol with not too great an excess of water. The bark when thus treated yields 10 to 12 p. c. of betulin (Hünefeld).

When the red-brown bark of *Betula alba* is exhausted with ether, the ethereal solution evaporated, and the amorphous yellow residue repeatedly boiled with water, there remains a brittle, yellowish-white, granular mass, which dissolves easily in ether, with difficulty in alcohol, and is insoluble in alkalis. It is inodorous and tasteless, melts slowly to a yellow oil, burns with an aromatic odour, and contains 80·00 p. c. C., 10·24 H., and 9·76 O. (Stähelin & Hofstetter, *Ann. Pharm.* 51. 79).

*Properties.* Very light white flocks, or crystalline nodules. Melts at about 200° (Hess), at 235° (Mason) to a colourless, transparent mass, with an odour like that of the heated bark. It sublimes in a current of air (Hess; Mason).

Betulin contains, on the average, 80·37 p. c. C., 10·98 H., and 8·65 O., from which numbers Hess calculates the formula $C^{40}H^{33}O^3$, Limpricht (*Lehrbuch*, 1037), the formula $C^{40}H^{32}O^4$. The formula $C^{90}H^{40}O^4$ or $C^{48}H^{36}O^4$ (calc. 80·9 p. c. C., 10·2 H.) agrees better with the analysis (Kr.). See also Heldt (*Ann. Pharm.* 63, 65).

*Decompositions.* Betulin volatilises on glowing charcoal in agreeably smelling vapours, and yields by *dry distillation*, first a white sublimate, then colourless water, a very viscid oil, resin, and charcoal. — It *burns* in a candle with white flame. — It dissolves rapidly but quietly in *oil of vitriol*, forming a solution which solidifies and turns white with water (Lowitz).

Betulin is insoluble in *water*. It does not combine either with *alkalis* (Lowitz; Hess) or with *acids*. According to Mason, it dissolves in aqueous alkalis, from which it is precipitated by acids.

It dissolves in 120 parts of cold, and 80 parts of hot *alcohol*, from which one-third is deposited on cooling (Lowitz). — It is soluble in *ether* (Mason), and easily in *acetate of ethyl, oil of turpentine*, and *almond oil* (Lowitz).

# Betuloretic Acid.

C. KÖSSMANN. *N. J. Pharm.* 26, 197; abstr. *Kopp's Jahresber.* 1854, 613.

Occurs as a white resinous meal covering the young shoots of the birch-tree, as well as the upper side of the young leaves, and is obtained therefrom by scraping. It is purified by dissolving it in boiling alcohol, evaporating the solution, exhausting the residue with ether, which leaves a black mass undissolved, evaporating the ethereal solution, dissolving the residue in carbonate of soda, and precipitating with an acid.

White flocks, or white friable mass, softening in the mouth, and melting perfectly at 94°. In alcoholic solution it is very bitter, and has an acid reaction. The soda-salt acts as a purgative. — It contains, at 100°, 74·43 p. c. C., 11·53 H., and 14·04 O., corresponding to the formula $C^{72}H^{66}O^{10}$ (by calc. 74·57 C., 11·42 H. (Kössmann).

Betuloretic acid is coloured a fine red by *oil of vitriol*, and forms a solution of the same colour : it does not form sugar even on prolonged digestion. When boiled with excess of nitric acid, it yields nitric oxide and picric acid.

The acid is insoluble in *water*. — It dissolves in aqueous *ammonia* and *potash*, and expels carbonic acid from alkaline carbonates. The precipitates obtained by double decomposition with metallic salts are insoluble.

*Soda-salt.* — Straw-yellow resin, soluble in water and alcohol. The aqueous solution is very bitter, and froths strongly.

*Lead-salt.* — White curdy precipitate, drying up to a yellow powder. It is decomposed by boiling with alcohol, a basic salt being formed.

*Silver-salt.* — Thrown down from the soda-salt in white flocks by nitrate of silver. It contains, at 100°, 16·56 p. c. AgO. (calc. for $C^{72}H^{65}AgO^{10}$ requires 16·97 p. c. AgO).

*Morphine-salt.* — The soda-salt precipitates acetate of morphine in the cold, and the hydrochlorate on boiling only. The latter precipitate is converted, on washing, into needles, from which sulphuric acid separates betuloretic acid.

*Quinine-salt.* — The soda-salt forms with sulphate of quinine a white precipitate, which is purified by dissolving it in boiling alcohol and evaporating the solution at 40°. — It forms an amorphous mass, soluble in alcohol and ether, and decomposible by dilute sulphuric acid, with separation of betuloretic acid.

The acid dissolves in *alcohol* and *ether*.

Concerning *Gummi Caja* see Peckolt (*N. Br. Arch.* 110, 44).

8. *Caranna.* From *Amyris Caranna, Bursera gummifera,* or *B. acuminata.* Dark-brown and green-brown, translucent at the edges ; at first tough, afterwards hard and brittle. Sp. gr. 1·124. It is easily fusible ; has a faint odour of gum ammoniacum in the cold, and an agreeable balsamic odour when heated ; tastes bitter and resinous. By distillation it yields a red, agreeably smelling oil. It contains 96 p. c. of a resin easily soluble in alcohol, ether, and potash. When submitted to dry distillation, it yields a pomegranate-yellow empyreumatic oil (Pelletier, *Bull. Pharm.* 4, 241).

9. *Resin of Ceradia furcata.* — Imported from Africa. — Amber-

yellow; smells like elemi. Sp. gr. 1·197. It dissolves in alcohol, forming a slightly acid solution, which is precipitated by water, but not by ammonia or nitrate of silver. — At 100° it emits a peculiar odour, softens, loses 10·6 p. c. in weight in a few days, and then contains 80·11 p.c. C., 9·79 H., and 10·00 O. (= $C^{40}H^{28}O^4$) (Robert Thomson, *Phil. Mag.* 28, 422).

10. *Resin of Ceroxylon Andicola.* — The *Cera de Palma* occurring in small yellowish-white pieces, obtained by boiling the shavings of the stem with water, contains a peculiar wax and a crystalline resin, separable by dissolving them in a large quantity of boiling alcohol, which deposits the wax first on cooling. The white resin which crystallises from the mother-liquor melts only above 100°, solidifying on cooling to a fissured amber-like mass, which dissolves slightly in cold, and easily in hot alcohol, also in ether and volatile oils. It contains 81·8 p. c. C., 11·5 H., and 5·1 O., corresponding to the formula $C^{40}H^{32}O^2$ (Boussingault, *Ann. Chim.* 29, 330 ; 59, 19).

# 11. Copal.

BERZELIUS. *Pogg.* 10, 254; *Lehrb.* 3 ed. 7, 53.
UNVERDORBEN. *Schw.* 59, 460.
FILHOL. *N. J. Pharm.* 1, 301 and 507 ; abstr. *Ann. Pharm.* 44, 323.
A. VOGEL, JUN. *N. Jahrb. Pharm.* 7, 370 ; *Kopp's Jahresber.* 1857, 484.
SCHILLER. *Ann. Pharm.* 113, 338 ; *Zeitschr. Ch. Pharm.* 3, 126 ; *Chem. Centr.* 1860, 414 ; *Kopp's Jahresber.* 1859, 515.

The Brazilian and West Indian copal is obtained from *Hymenea Courbaril,* the African and East Indian from *Hymenea verrucosa,* or from *Elæocarpus copaliferus,* the North American from *Rhus copallina.*

Copal occurs as a hard and as a soft resin, exhibiting, according to Werlé (*Pharm. Viertelj.* 14, 86), the following varieties :—

A. *Hard kinds.* 1. *Copal from Zanguebar.* The so-called East Indian, Bombay, or Salem copal of commerce. It is dug up from the earth in Eastern Africa, and transported across Zanguebar. — In the crude state it usually occurs in dull flat pieces, from the size of a bean to that of the hand, covered with sand and earth. After proper washing, it forms colourless or brownish-red, clear and transparent pieces, having elevations of the size of pins' heads on the surface. It has a partly dull, partly glassy fracture, splinters when cut, and is susceptible of being ground and polished. It is nearly as hard as amber.

2. *Copal from Sierra Leone.* — Either perfectly clear globules or drops, seldom larger than a nut (glass copal), or flat, conchoïdal, colourless, glassy pieces, often covered with earth, and having vegetable remains imbedded in them. Nearly as hard as 1.

3. *Copal from Benguela.* — Clear, pale-yellow, seldom colourless pieces, of all sizes and thicknesses, generally conchoïdal, and never globular or disc-shaped. Has a glassy fracture. In the crude state it is covered with a whitish-yellow crust of lime.

4. *Copal from Angola.* — Regular, reddish golden-yellow pieces, generally globular in form, having warts on the surface larger than in the first variety. Much softer than 1, and covered, in the rough state, with a thick red crust.

B. *Soft kinds.* 5. West Indian or *Ball copal.* Mostly from the west coast of Africa, more rarely from the West Indies, Brazil, and Central America. Tears and conglomerated pieces from the size of a bean to that of the fist, generally covered with a film of lime. Milky, or oftener clear and colourless. Very soft, so that when rubbed on wool, it wears off and becomes sticky. More easily fusible than the previous kinds. Occurs in commerce in several varieties.

6. *Kaurie copal.* From New Zealand. In masses weighing as much as 100 pounds, with grey calcareous crust, opaque within; in thin splinters, transparent with grey or brown colour. Harder than 5; easily fusible.

7. *Manilla copal.* From living plants. A hard and a soft variety occur in commerce. The hard variety resembles 6, but is darker, of a yellow to brown colour, harder and less easily fusible. — The *soft* variety forms conglomerated masses of tears or blocks, frequently mixed with vegetable remains and earth, of a dirty to pure yellow colour, pulverisable between the fingers in small pieces. It dissolves in alcohol before melting.

On the varieties of copal see further Martius (*Repert.* 26, 295); Schindler (*J. pr. Chem.* 4, 149); Giseke (*N. Br. Arch.* 18, 180); Perottet (*N. J. Pharm.* 1, 406); Guibourt (*Rev. Scient.* 16, 177); Batka (*N. Tr.* 23, 2, 83).

Sp. gr. 1·069 (Thomson), 1·045 to 1·139 (Boisson). Tasteless; emits a faint odour when rubbed.

|  |  |  | Filhol. |  |  |  | Schibler. |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | Calcutta. |  | Bombay. |  | Madagascar. |  | Manilla. |  | Africa. |
| C | 80·66 | ........ | 79·7 | ........ | 79·80 | ........ | 79·35 | ........ | 79·62 |
| H | 10·57 | ........ | 9·9 | ........ | 10·78 | ........ | 10·27 | ........ | 10·32 |
| O | 8·77 | ........ | 10·4 | ........ | 9·42 | ........ | 10·38 | ........ | 10·06 |
|  | 100·00 | ........ | 100·0 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Filhol dried his copal at 100° in a current of hydrogen.

Copal absorbs oxygen rapidly from the *air*, and afterwards contains a smaller per-centage of carbon, and is more soluble in alcohol, ether, and oil of turpentine than before. Pulverised Calcutta copal containing 80·4 p. c. of carbon, after being heated to 100° for three days in a current of air, contains 76·54 p. c. of carbon; the powder, after keeping for a month, is almost entirely soluble in alcohol, and then contains 73 p. c. of carbon. Durozier's *soluble copal* is a product of this kind, obtained by triturating hard Indian copal with water, and preserving it in contact with air; it contains 71·38 p. c. C., 9·23 H., and 19·47 O., is perfectly soluble in alcohol, ether, and oil of turpentine, but still consists of a mixture of several resins (Filhol). — Copal melts when *heated*, evolving an aromatic odour, and giving off water and a little volatile oil, after which it does not undergo much alteration, a small quantity only of a resin soluble in potash and oil of turpentine, and insoluble in alcohol, being produced (Unverdorben). Hard copal

melts at 340°, that of medium hardness at 180° (Violette). When more strongly heated it froths up for a while, giving off an oil (A), and afterwards flows quietly; it still, however, contains a large quantity of undecomposed copal (Unverdorben), and is not yet soluble in cold or hot oil of turpentine, in which it dissolves only when 20 to 25 p. c. has been distilled off at a temperature of 360°. Turpentine which has become thickened by exposure to air and light, however, dissolves copal which has lost 10 p. c. by distillation (Violette, *Repert. Chim. appl.* 1862, 329; *Chem. Centr.* 1863, 639). — Copal which has been heated till it has become soluble in oil of turpentine consists of (1) unchanged alpha- and beta-resin; (2) a small quantity of a resin resembling beta-resin, easily soluble in ether and oil of turpentine, but soluble only in 50 parts of boiling alcohol, and deposited from the latter solution, on cooling, in the form of a tarry alcoholate; (3) two newly-formed resins, one of which resembles the delta-resin, but is soluble in oil of turpentine, whilst the other dissolves also in aqueous ammonia, and in absolute and 80 p. c. alcohol, ether, and fatty oils. — If the melted copal be distilled till only 8 p. c. remains, the oil B passes over, the residue consisting of a mixture of various resins (Unverdorben). The two oils of copal, A and B, contain: A. Easily volatile and difficultly volatile oil, acetic acid, empyreumatic acid (*Brandsäure*), and a large quantity of resin soluble in alcohol and potash. — B. Easily and difficultly volatile oil, acetic acid, and two resins, one of which is soluble in ether and alcohol, the other (the *Brandsäure* of Unverdorben) being white, oily, of penetrating empyreumatic odour, acid, and precipitable from its alkaline solution by excess of caustic potash, and from the alcoholic solution by acetate of copper, the latter precipitate dissolving in ether (Unverdorben).

The oil obtained by the distillation of Manilla copal on the large scale is dark-brown; that distilled from African copal at a higher temperature in copper vessels is coloured green by the copper. When the oil is rectified, a black pitch remains behind; the distillate, shaken with caustic potash (which takes up copallic acid), subjected to fractional distillation, and set aside for a month with pieces of caustic potash in the separate portions, is resolved into three products: $a$, a hydrocarbon of the formula $C^{20}H^{16}$ and sp. gr. 0·951 at 10°; $b$, a portion distilling at 165° to 215°, and containing 84·53 p. c. C., 11·32 H., and 4·15 O.; and $c$, a thick yellow oil boiling at 215° to 260°, and containing, on the average, 74·18 p. c. C., 10·23 H., and 15·59 O. Besides these the distillate contains an acid which is removed by shaking with water (Schibler's *copalic acid*), and, when combined with oxide of lead and again separated by means of hydrosulphuric acid, dries up to a red-brown mass containing needles. The baryta-salt forms a reddish-brown syrup (Schibler).

No hydrosulphuric acid (Baudrimont) or umbelliferone (Sommer) is obtained by the dry distillation of copal.

*Oil of vitriol* dissolves copal, forming Hatchett's artificial tannin: *nitric acid* also dissolves and decomposes it.

Copal is not dissolved by trituration with *water*, but its oxidation is promoted thereby (Filhol). When it is distilled with water, a very small quantity only of a volatile oil having a smell of copal is obtained (Unverdorben). — Copal is not soluble in *liquid carbonic acid* (Gore), and only partially soluble, with evident alteration, in *bisulphide of carbon* (Lampadius).

Powdered copal, moistened with aqueous *ammonia*, and set aside in a closed vessel in a warm place, swells up to a clear jelly, which yields with a little water, a turbid, viscid, slimy mass, and with a large quantity a milky liquid. On evaporation there remains, first a white tough elastic mass, and on further drying at 40° to 60°, a yellowish fused mass, which remains soft at this temperature for some weeks, but is hard and brittle in the cold, and dissolves very slightly in boiling alcohol. On the other hand, the jelly produced by ammonia mixes directly with alcohol to a clear liquid, with the exception of the not sufficiently swelled copal, which remains behind and cannot be dissolved by a larger quantity of ammonia. The alcoholic solution of the jelly leaves on evaporation a white earthy pellicle, which softens to a transparent varnish at 40°. — From the solution of copal in aqueous potash sal-ammoniac throws down white flocks, which do not dissolve in boiling alcohol, even on addition of ammonia (Berzelius).

East Indian copal moistened with ammonia and set aside, according to the method of Berzelius, remains pulverulent for several days, but swells up, on addition of hot alcohol, to a translucent jelly, which yields a clear filtrate when thrown on a filter, but does not itself dissolve (Filhol).

Copal dissolves in hot *caustic potash* (Hatchett) emitting an aromatic odour, but being first converted into a clear ropy mass. The clear yellowish solution becomes turbid and white on cooling and afterwards curdles, with separation of a little yellowish liquid, which contains one resin, whilst the jelly contains another resin in combination with potash. If the resin be separated from the jelly by means of an acid, white flocks are obtained, which do not cohere on heating the liquid to 40°: the yellowish liquid yields with acids a resin which cakes together in the cold (Berzelius). East Indian copal does not dissolve in cold caustic potash, and floats on the boiling liquid as a spongy curdled mass, which does not dissolve for some hours : from the alkaline liquid acids throw down only a few flocks, whether weak or strong caustic potash has been employed (Filhol). — Copal powder moistened with alcoholic potash assumes a dark-red colour in the air (Filhol). — Copal boiled with aqueous carbonate of potash softens without dissolving (Berzelius).

The solution of copal-potash precipitates the salts of the earths and alkaline earths : the precipitates are white or yellowish, hard and earthy after drying. The salts of the heavy metals are likewise precipitated (Berzelius).

Copal dissolves freely in *chloroform* (Cloëz). — It dissolves but slightly in absolute *alcohol*, and is nearly insoluble in weaker spirit : according to some authorities, it dissolves more freely when lumps of the copal are suspended in alcohol-vapour, or when camphor is added to the alcohol, a statement which was not confirmed for all kinds of copal by the experiments of Berzelius. Copal swells up to a tough elastic body in boiling absolute alcohol. — According to Unverdorben, copal dissolves completely when digested with 1½ parts of alcohol for 24 hours, the solution first formed acting as a solvent of the portion insoluble in alcohol alone. According to Filhol, East Indian copal does not dissolve in this way.

Copal powder swells up in *ether* to a bulky jelly, which, according to Bonastre and Filhol, dissolves slightly, but according to Pfaff and Berzelius, completely, in excess of ether   When ether containing gela-

tinous copal is heated to boiling and shaken with a small quantity of warm alcohol, a transparent liquid is obtained, which may be diluted at pleasure, whilst a large quantity of cold alcohol added at once causes the solution to curdle (Berzelius). Ether containing iodine dissolves copal completely after some time (Vogel). — Powdered copal heated till it begins to melt, dissolves in about 2·8 parts of anhydrous *acetone*, forming a solution from which a part may be distilled, leaving a syrupy liquid : on complete evaporation a brittle varnish remains (Wiederhold, *Polyt. Notizbl.* 19, 214). — *Valerianic acid, fusel oil, valerianic aldehyde*, and *valerate of amyl* cause East Indian copal to swell up to a translucent mass (Trautwein). — With a little *carbolic acid*, copal deliquiesces at 18° to an elastic varnish, which dissolves almost completely in a larger quantity of the acid, forming a solution which mixes with warm alcohol (Runge, *Pogg.* 32, 322).

Copal dissolves slowly in *benzene*, better when it is suspended in the vapour of the boiling liquid, the solution then running off in drops of colourless varnish (Mansfield). *Rock oil* dissolves scarcely 1 p. c. of copal (Saussure). *Oil of turpentine* acts in a similar manner, but dissolves a larger quantity when it is made to act in the state of vapour, or when it is heated above its boiling-point with the copal in closed vessels, or when aqueous ammonia is added ; the last process, however, yields a varnish which dries with difficulty. — Volatile oils cause copal to swell, and dissolve a portion, but never the whole (Filhol). — Cold *oil of cajeput* dissolves copal ; the solution leaves a shining varnish on evaporation (Draper, *Chem. News*, 1862, 184 ; Palm, *Pharm. Viertelj.* 11, 555). The oil obtained by the dry distillation of copal dissolves soft and semi-hard copal (Violette).

Copal dissolves in the mixture of *oleic* and *stearic* acids separated from soap by acids (Hausmann, *Ann. Chim.* 18, 185). — It appears to dissolve in fatty oils, such as *linseed* oil, only after it has been melted till it no longer evolves acid aromatic vapours. — It dissolves in *castor oil* to a yellow liquid, which mixes with hot alcohol, and deposits a part of the copal on cooling : the mixture with ether also deposits copal after some time (Stickel, *J. pr. Chem.* 9, 166). On the preparation of copal-varnish see Giseke (*N. Br. Arch.* 18, 186), Böttger (*J. pr. Chem.* 12, 253).

*Separation of the Resins of Copal.* A. *According to Unverdorben.* Powdered African copal is exhausted with the following liquids in succession : 1. Alcohol of 67 p. c. ; 2. absolute alcohol ; 3. boiling alcohol of 77 p. c., with the addition of half the weight of the residue of caustic potash ; 4. alcohol of 25 p. c.

1. The solution in 67 p. c. alcohol contains alpha- and beta-resin. It is precipitated by alcoholic acetate of copper, and the precipitate is treated with ether, which dissolves the copper-compound of the alpha-resin, but leaves that of the beta-resin as a green powder. The resins are separated from oxide of copper by dissolving the compounds in alcohol containing hydrochloric acid, and precipitating with water.

*Alpha-resin.* Soft and flexible from the presence of volatile oil, which may be removed by fusion at a gentle heat. White and shining ; softens in the mouth ; melts at 100°. Dissolves to a slimy liquid in ammonia, and is not completely precipitated by boiling for a short time. — It dissolves in caustic potash without coloration ; excess of potash

throws down a tarry precipitate, difficultly soluble in cold, but easily soluble in boiling water. — The potash-salt produces with chloride of barium a precipitate, which is insoluble in alcohol and ether, and cakes together in a resinous mass on boiling. It precipitates the salts of the earths and heavy metals. The copper-salt dissolves easily in ether, and is decomposed by acetic acid. — From the alcoholic solution of the resin, water throws down a transparent oil, which gives up its alcohol when boiled with caustic potash, but not on boiling for a short time alone.

*Beta-resin.* Resembles the alpha-resin, but dissolves only in absolute alcohol, and forms with baryta, sesquioxide of iron, and copper salts insoluble in ether. It forms with alcohol of 67 p. c. a white oily alcoholate, which loses its alcohol when boiled with water, remaining porous and brittle : with ammonia it forms a thick clear solution, which loses its ammonia by boiling. The ammoniacal solution dries up in the air to a fissured ammoniacal resin. — The beta-resin dissolves easily in caustic potash, an excess of potash throwing down a precipitate, which is soluble in water and alcohol, but insoluble in ether. — It dissolves in ether, but not in oil of turpentine or fat oils.

2. The solution obtained with absolute alcohol contains alpha-, beta-, and gamma-resin, the last two precipitable by excess of alcoholic caustic potash. On dissolving the precipitate in water, decomposing it with hot dilute sulphuric acid, and treating the separated resin with cold absolute alcohol, the gamma-resin remains behind undissolved. — The same gamma-resin occurs in the solution prepared with 77 p. c. alcohol and caustic potash, and is precipitated therefrom by sulphuric acid.

*Gamma-resin.* — White meal, which cakes together when heated, melts only at 350° in closed vessels, frothing up strongly, and being converted into a resin soluble in oil of turpentine. It is insoluble in ammonia-water, except on addition of alcohol. The concentrated solution in caustic potash is a thick liquid, which leaves on evaporation a transparent gum, soluble in water only after addition of alcohol, and precipitable from the solution by excess of potash. The potash-compound of the resin dissolves in absolute alcohol ; it throws down from metallic salts gelatinous precipitates, which are insoluble in alcohol, ether, and oils. — The gamma-resin does not dissolve in absolute alcohol, but converts it into a transparent, tarry alcoholate. It dissolves easily in ether, and in oil of cajeput and other oils, but not in oil of turpentine.

3. The extract of the copal-residue obtained with alcohol of 25 p. c. deposits, when mixed with hydrochloric acid, a jelly of the delta-resin, which is converted into a white mealy hydrate by boiling.

*Delta-resin.* — Loses a little water at 100°, and more at 300°, runs together without melting, and carbonises when more strongly heated. By prolonged heating, a resin soluble in oil of turpentine is obtained. — The delta-resin does not dissolve in aqueous or alcoholic ammonia, if other resins are not present. Aqueous potash converts it into a potash-compound, which is insoluble in water, but soluble in weak alcohol. — The copper-salt is insoluble in ether and oils, and the resin itself is insoluble in absolute alcohol, ether, and oil of turpentine.

4. The portion of copal remaining undissolved after the whole of the foregoing treatment, amounts to about 8 per cent., consisting of *epsilon-resin*. It behaves like the delta-resin when heated, giving off its water, and caking together in a dense mass. It is insoluble in ether, alcohol, and oils. — When the delta- and epsilon-resins are kept under alcohol in a flask containing air, they are converted for the most part into soluble resins. This conversion seems to take place also in copal when kept (Unverdorben).

B. *According to Filhol.* Filhol, by treating East Indian copal according to Unverdorben's method, also obtained five resins, which, however, only partially correspond with those obtained by Unverdorben.

1. When the solution obtained with boiling alcohol of 67 p. c. is precipitated by alcoholic acetate of copper, and the precipitate is collected and dried, first at 40° to 50°, and afterwards at 100°, without access of air, it gives off water and a volatile oil, becoming translucent and friable. On treating it with cold ether, a compound of alpha-resin with oxide of copper, which forms the chief part of the precipitate, is dissolved; the insoluble residue contains several resins, but is of very small amount. — The alcoholic solution from which the alpha-resin has been precipitated by acetate of copper contains the copper-compound of Filhol's beta-resin, which differs therefore from Unverdorben's beta-resin.

*Alpha-resin.* — Separated from the copper-compound by Unverdorben's method. Or the solution in alcohol containing hydrochloric acid is precipitated with excess of hydrosulphuric acid, the filtrate evaporated, and the remaining resin purified by again dissolving it in cold weak spirit and drying it at 100°, whereby a volatile oil is expelled. — The resin thus obtained is brittle, translucent, of lemon-yellow colour, fusible at 100°, completely soluble in alcohol of 72 p. c., also in absolute alcohol, ether, and oil of turpentine. Its salts dissolve in ether but not in alcohol, with the exception of the ammonia-salt, which dissolves easily in alcohol, and gives off the whole of its ammonia only on long boiling. The potash-salt is insoluble in alcohol containing potash, and is precipitated from its aqueous solution by the slightest excess of potash. The alcoholic solution of the resin throws down gelatinous precipitates from salts of the heavy metals; the copper-salt is blue and insoluble in alcohol. — The lead-salt, precipitated from the alcoholic resin by an insufficient quantity of alcoholic neutral acetate of lead, contains 26·24 p. c. of oxide of lead.

| | | | | Filhol. | | | |
| | | | | | | In the | |
| *Calculation according to Filhol.* | | | | Uncombined. | | lead-compound. | |
| 40 C | 240 | | 77·17 | | 76·87 | | 76 87 |
| 31 H | 31 | | 9·94 | | 10·16 | | 10·11 |
| 5 O | 40 | | 12·89 | | 12·97 | | 13·02 |
| $C^{40}H^{31}O^5$ | 311 | | 100·00 | | 100·00 | | 100·00 |

On the formulæ of this and the other resins of copal, see Heldt (*Ann. Pharm.* 63, 68).

*Beta-resin.* — Obtained by precipitating the alcoholic solution of its copper-salt with hydrosulphuric acid, filtering, and evaporating. Or

the alcoholic solution is mixed with hydrochloric acid, and the resin precipitated by a large quantity of water; in this way, however, an emulsion is easily formed, from which the resin separates only on boiling off the alcohol. In either case the resin is washed with boiling water and again dissolved in cold weak spirit. It still contains volatile oil, which is removed by prolonged boiling with water, or by drying at 100° in a current of hydrogen. It resembles the alpha-resin, and, like it, contains 76·95 p. c. C., 10·05 H., and 13·00 O., but forms with bases compounds soluble in alcohol and ether. The ammonia and potash-salts are viscid and sticky; the latter is insoluble in alcohol containing potash. Since alcoholic neutral acetate of lead does not precipitate solutions of the resin, the lead-salt is obtained by prolonged fusion of the resin with excess of lead-oxide, extraction with alcohol, and evaporation. It is transparent and fusible, and contains 25 to 28 p. c. of oxide of lead. The copper-salt is of a fine green colour, melts about 100°, and remains transparent on cooling.

2. The copal which has been exhausted with 67 p. c. alcohol gives up to boiling absolute alcohol a further quantity of alpha- and beta-resin, and also gamma-resin. The solution is precipitated by alcoholic acetate of lead, and the precipitate, which contains alpha- and gamma-resin, is dried and exhausted with ether, which leaves the copper-compound of the gamma-resin undissolved.

*Gamma-resin.* White, very light powder, which melts with difficulty, undergoing decomposition. It remains behind as a transparent slightly coloured resin on evaporating its alcoholic solution. Oxidises in the air. — The potash-salt is sticky, slightly soluble in water, moderately soluble in alcohol, soluble also in alcohol containing potash. — The salts of the metals are insoluble in alcohol and ether. The lead-salt is a heavy, fusible, white powder; the copper-salt is blue, resembling the acetate.

|  |  | *Calculation according to Filhol.* |  |  | Filhol. mean. |
|---|---|---|---|---|---|
| 40 C | 240 | ............ | 81·35 | ............ | 80·62 |
| 31 H | 31 | ............ | 10·50 | ............ | 10·54 |
| 3 O | 24 | ............ | 8·15 | ............ | 8·84 |
| $C^{40}H^{31}O^4$ | 295 | ............ | 100·00 | ............ | 100·00 |

3. The soft elastic residue remaining from the previous treatment of copal dissolves partially in alcoholic potash; from the filtrate dilute sulphuric acid throws down a large quantity of gamma-resin with a little delta-resin. Alcohol of 25 p. c. then dissolves the remainder of the delta-resin as a potash-compound, leaving the indifferent and insoluble epsilon-resin. To separate the gamma- and delta-resins they are treated, after drying, with anhydrous alcohol containing ether, which dissolves only the gamma-resin.

*Delta-resin.* — Present in small quantity only. Gelatinous, or after drying, a white powder. Melts only when strongly heated, undergoing decomposition. It is soluble in alcoholic potash, but not in alcohol or ether.

*Epsilon-resin.* Transparent gelatinous mass, drying up to small hard granules, insoluble in all liquids.

|  |  | Calculation according to Filhol. |  |  | Filhol. mean. |
|---|---|---|---|---|---|
| 40 C | 240 | ............ | 83·62 | ............ | 81·42 |
| 31 H | 31 | ............ | 10·81 | ............ | 10·48 |
| 2 O | 16 | ............ | 5·57 | ............ | 8·10 |
| $C^{40}H^{31}O^2$ | 287 | ............ | 100·00 | ............ | 100·00 |

C. *According to Vogel.* Vogel distinguishes only two resins in copal, the one soluble, the other insoluble, in alcohol. Transparent copal containing 78·13 p. c. C., 10·46 H., and 11·41 O., gave up to 90 p. c. alcohol, 38 p. c. of soluble resin containing 77·70 p. c. C., 10·72 H., and 11·58 O. The insoluble resin contained 78·59 p. c. C., 10·08 H., and 11·33 O., and from another copal, 76·12 p. c. C., 11·11 H., and 12·77 O.; it was not altered or blackened by digestion with oil of vitriol for 24 hours. It dissolves in ether, the solution yielding, on evaporation, a varnish which is insoluble in alcohol, but becomes soluble in that liquid when exposed to the air for some months.

## 12. Elemi-resin.

JOHN. *Berl. Jahrb.* 1819, 356.
BONNASTRE. *J. Pharm.* 8, 388 ; *N. Tr.* 7, 1, 368. — *J. Pharm.* 8, 574 ; 9, 179 ; 10, 198.
H. ROSE. *Pogg.* 33, 49 ; 48, 61 ; also *J. pr. Chem.* 18, 321. — *Pogg.* 53, 364.
JOHNSTON. *Phil. Trans.* 1840, 361.
HESS. *Ann. Pharm.* 29, 137 ; *J. pr. Chem.* 16, 162 ; *Pogg.* 46, 320. — *J. pr. Chem.* 19, 508 ; *Pogg.* 49, 219.
SCHRÖTTER. *Pogg.* 59, 68.
BAUP. *N. J. Pharm.* 20, 321 ; *Ann. Pharm.* 80, 312 ; *J. pr. Chem.* 55, 83.

Obtained from various species of *Amyris* or *Icica* (Handbuch, viii, [2], 19). Occurs in commerce as West Indian and East Indian elemi. — The West Indian resin forms brittle, opaque masses of lemon-yellow or greenish colour, softening between the fingers, and easily fusible. Sp. gr. 1·018 (Brisson), 1·083 (Pfaff). Its alcoholic solution reddens litmus (Bouillon-Lagrange & Vogel). Elemi does not yield umbelliferone by dry distillation (Sommer), and when it is melted with hydrate of potash, neither phloroglucin nor protocatechuic acid is formed (Hlasiwetz & Barth). It softens when warmed with nitric acid, and dissolves on boiling, forming camphretic acid and the decomposition-products of gum and albumin (Schwanert, *Ann. Pharm.* 128, 124). It dissolves in hot alcohol, with the exception of impurities, and partly in creosote (Reichenbach). — Yellowish-white, dull, brittle pieces had a sp. gr. of 1·055 at 208, became soft at 80°, melted to a limpid yellow oil at 120°, and contained 78·72 p. c. C., 10·71 H., and 10·57 O. (Schrötter).

Elemi contains a volatile oil (xiv, 289), a resin easily soluble in cold alcohol, and a resin soluble only in hot alcohol, besides extractive matters (Bonastre). Johnston and Rose also found only two resins in elemi, whereas John and Baup seem to have distinguished three resins.

John found a soft resin, a second resin soluble only in ether, and a third soluble in hot alcohol and crystallising on cooling. According to Baup the portion insoluble in cold alcohol is amyrin (p. 397); the soluble portion contains an amorphous resin and *Elemin*, which latter body forms six-sided prisms, melting about 200°, and soluble in 20 parts of cold 88 p. c. alcohol (Baup).

a. *Sparingly soluble Resin of Elemi*. — Obtained by exhausting elemi repeatedly with cold alcohol and dissolving the residue in boiling alcohol, from which the resin is deposited on cooling (Bonastre ; Rose). — Pure white, indistinctly crystalline flocks (Rose). Stellate groups of crystals, especially fine from alcohol containing volatile oil of elemi (Bonastre). Colourless crystals, melting at 149° to a colourless oil, which solidifies to a brittle resin on cooling (Johnston). Neutral.

|          |       |        |       | Rose. mean. |        | Hess. |        | Johnston. at 93°. |
| -------- | ----- | ------ | ----- | ----------- | ------ | ----- | ------ | ----------------- |
| 40 C     | 240   | ...... | 85·41 | ......      | 84·45  | ...... | 84·20 | ...... 84·01      |
| 33 H     | 33    | ...... | 11·74 | ......      | 11·77  | ...... | 11·53 | ...... 11·87      |
| O        | 8     | ...... | 2·85  | ......      | 3·78   | ...... | 4·27  | ...... 4·02       |
| $C^{40}H^{33}O$ | 281 | ...... | 100·00 | ......   | 100·00 | ...... | 100·00 | ...... 100·00    |

Probably identical with the crystals of animé resin (Hess).

Elemi-resin burns with flame when *heated*, evolving a resinous odour. — When submitted to dry distillation, it yields an acid thick distillate (Rose). — It does not alter when hydrochloric acid gas is passed over it (Rose).

*Combinations*. — *With Water ?* When crystallised elemi is dissolved in so much alcohol that nothing is deposited on cooling, and the solution is evaporated in a vacuum or at a very gentle heat, the liquid deposits, besides the needles, amorphous, glassy, often yellowish-coloured masses, which scarcely lose weight over the water-bath. These masses, not completely separated from the crystalline resin, were analysed by Rose, who found them to contain much less carbon than the crystals (frequently not more than 80 p. c., and sometimes only 76 to 40 p. c.); according to him, they are formed by the combination of the crystals with water. Other glassy masses, however, contained 82 p. c. of carbon, so that the existence of a hydrate appears doubtful. Elemi is insoluble in water and does not combine with *bases*. The alcoholic solution forms a jelly with ammonia ; it is not rendered turbid by caustic potash. Alcoholic *neutral acetate of lead* and *nitrate of silver* produce no precipitate, even on addition of a little ammonia (Rose).

Elemi dissolves in boiling *alcohol*, and is deposited from the solution on cooling in the form of a jelly or a spongy mass (Bonastre). The alcoholic solution turns milky on cooling and afterwards deposits crystals (Rose). It dissolves easily in *ether*, from which it crystallises ; also in *oil of turpentine ;* less easily in *oil of almonds* (Bonastre).

b. The portion of elemi-resin soluble in cold alcohol is brownish-yellow, brittle, and transparent, and has a smell of lemons. It becomes white and opaque when boiled with water, but does not colour the water. It combines with bases (Johnston). — Contains, at 100°, 77·57 p. c. C., 10·43 H., and 12·00 O. (Johnston). Contains 75·39 p. c. C.,

11·89 H., and 12·72 O. (Rose). According to Johnston it is represented by the formula $C^{40}H^{32}O^4$.

13. IVY-RESIN. — From *Hedera Helix*. Red-brown or greenish, transparent, brittle pieces, of sp. gr. 1·294 according to Brisson. Has a faint aromatic smell and an aromatic acrid taste. Contains 23 p. c. of resin, 7 of gum, and 70 of woody fibre, together with malic acid and salts (Pelletier, *Bull. Pharm.* 4, 504). It burns with a bright flame, emitting an agreeable odour. When subjected to dry distillation, it yields, first acid, then ammoniacal water, and a yellow and red oil (Geoffroy). No umbelliferone is obtained thereby, or when the resin is carbonised by oil of vitriol and boiled (Sommer, *N. Br. Arch.* 98, 11).

14. EUPHORBIUM. — From *Euphorbia officinarum*, *E. antiquorum*, and *E. canariensis*. Yellowish or brownish externally and whitish within; brittle, often hollow pieces, softening when warmed. The resin is without smell, but the dust excites sneezing; when chewed it has an acrid and persistent burning taste. It does not yield umbelliferone by dry distillation (Sommer). — It contains a brittle, poisonous resin, soluble in alcohol, ether, and oil of turpentine, and slightly soluble in ammonia-water and warm caustic potash (Braconnot; Brandes), besides gum, wax, caoutchouc, and malic acid and its salts. See Braconnot (*Ann. Chim.* 68, 44), Pelletier (*Bull. Pharm.* 4, 502), Brandes (*Repert.* 6, 145), Buchner & Herberger (*Repert.* 37, 213).

The *easily soluble portion of euphorbium resin* is obtained as a brown-yellow resin by extracting with cold alcohol and evaporating the pale-yellow solution. When boiled with water, it turns pale-yellow and opaque, and colours the water pale-yellow. When dried at 100°, it again becomes transparent, brown-red, and semi-fluid, cooling to a brittle mass. It contains 74·03 to 75·26 p. c. C., 9·83 to 10·20 H., and 15·14 to 14·54 O., but probably still contains some of the sparingly soluble resin (Johnston, *Phil. Trans.* 1840, 364).

The *sparingly soluble resin* crystallises in radiated hemispherical tufts, becomes luminous when rubbed, but loses this property after being rubbed for some time, and does not again crystallise from alcohol (Bonastre). — According to Rose, on the contrary, the sparingly soluble resin is deposited from the hot alcoholic solution, on cooling, in amorphous starchy masses, which contained on one occasion 80·20 p. c. C., 11·12 H., and 8·68 O., and on another occasion 78·55 p. c. C., 10·96 H., and 10·49 O. The alcoholic solution reddens litmus and has a faintly acrid taste; it is not precipitated by alcoholic potash, neutral acetate of lead, or nitrate of silver, even after addition of a little ammonia. Aqueous potash turns it turbid, and aqueous ammonia throws down a white precipitate without forming a jelly. — When euphorbium is boiled for a long time in alcohol, no deposit takes place on cooling; the solution, evaporated in a vacuum, leaves a transparent turpentine, in which opaque white masses, less rich in carbon (77·29 and 78·64 p. c.) than the sparingly soluble resin, are formed on standing (Rose, *Pogg.* 33, 52; 53, 369).

See John on the resin of *Euphorbia Cyparissias*, and Ricord Madianna on the milky juice of *Euphorbia myrtifolia* (*J. Pharm.* 18, 589).

15. GOMART-RESIN from *Bursera gummifera*. Solid dry resin, white and of crystalline texture, somewhat soft within, and exhibiting hollows lined with shining crystalline nodules. It melts with difficulty, and

breaks up into sticky granules in boiling water. It has an odour between those of elemi and turpentine. When distilled with water it yields a volatile oil (xiv, 291).

16. GAMBOGE. *Gummigutt.* That obtained from *Hebradendron cochinchinense* alone occurs in commerce in pipes, cakes, and as ordinary gamboge. [See Hanbury (*N. Repert.* 14, 1)]. Cylindrical masses $\frac{3}{4}$ to 3 inches in diameter, or thick cakes a pound in weight. It is of a dirty yellowish-brown colour, dusty on the surface, and has a smooth, shining, conchoïdal fracture. Brittle, and triturable to a fine yellow powder. Inodorous, tastes slight at first, and afterwards harsh and acrid; colours the saliva yellow. Softens when heated, without melting. It kindles in a flame, and burns with a smoky flame. Forms with water a fine yellow emulsion, and dissolves in alcohol and ether, leaving gum.

Gamboge, melted with hydrate of potash, yields protocatechuic acid and phloroglucin (Hlasiwetz & Pfaundler, *Wien. Acad. Ber.* 50, 52), together with acetic acid (propionic and butyric acids), and a sparingly soluble resin resembling that obtained from benzoïn (p. 383) (Hlasiwetz & Barth, *Ann. Pharm.* 134, 281). It does not yield umbelliferone by dry distillation (Sommer).

Pipe gamboge contains 72 p. c. of gamboge-yellow, 23 p. c. of gum, and 5 of water: the other kinds generally contain less yellow, and also starch and woody fibre (Christison). See the analyses of Braconnot (*Ann. Chim.* 68, 33), John (*Chem. Schriften*, 4, 190), Christison (*Ann. Pharm.* 19, 221; complete: 23, 172; abstr. 76, 343), Büchner (*Ann. Pharm.* 45, 72).

## Gamboge-yellow.

BRACONNOT. *Ann. Chim.* 68, 36.
JOHN. *Chem. Schriften*, 4, 193.
UNVERDORBEN. *N. Tr.* 8, 1, 60.
CHRISTISON. *Ann. Pharm.* 23, 185.
JOHNSTON. *Phil. Trans.* 1839, 281.
PH. BÜCHNER. *Ann. Pharm.* 45, 72.

*Resinous Gamboge-yellow. Gambodic acid* (Johnston). — Chiefly investigated by Johnston and Büchner, but with not perfectly concordant results.

*Preparation.* 1. Gamboge is exhausted with absolute ether, the dark-yellow solution is evaporated, and the remaining hyacinth-red transparent mass, which gives off the last portions of ether only at a high temperature, is heated till it becomes hard and brittle (Christison; Johnston). — Gamboge is exhausted with alcohol and the solution precipitated by water. — 3. Gamboge is exhausted with potash and the solution precipitated by hydrochloric acid (Johnston). — The yellow extracted by ether contains a little lime: if it be dissolved in potash and precipitated by hydrochloric acid, it takes up a little potash which cannot be removed by washing. The yellow precipitated from an ammoniacal solution by hydrochloric acid is free from ash, but contains water (Buchner).

*Properties.* Cherry-red or nearly opaque mass, triturable to a fine yellow powder. Inodorous; tasteless; has an acid reaction. — The yellow precipitated from an ammoniacal solution, when kept for some

time at 100°, melts to an opaque viscid mass, which loses a large quantity of water at a higher temperature, becoming thinner, and is cracked and brittle after cooling (Büchner). — It does not undergo any alteration at 177° (Johnston).

| Calculation according to Johnston. | | | | | Johnston. mean, at 100°. | | Büchner. mean. |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 40 C | 240 | ........ | 73·17 | ........ | 71·53 | ........ | 72·05 |
| 24 H | 24 | ........ | 7·32 | ........ | 7·29 | ........ | 7·23 |
| 8 O | 64 | ........ | 19·51 | ........ | 21·18 | ........ | 20·72 |
| $C^{40}H^{24}O^8$ | 328 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Johnston gives also the formula $C^{40}H^{24}O^9$. Büchner gives for the yellow in the salts the formula $C^{60}H^{35}O^{12}$: he seems to take 6·12 as the atomic weight of carbon.

*Decompositions.* — Gamboge-yellow gives off white vapours at 204°, turning darker, and afterwards contains 72·79 p. c. C., 6·60 H., and 22·61 O. When this body is treated with alcohol, about half remains undissolved in the form of a yellow powder, which contains 70·70 p. c. C., 7·03 H., and 22·27 O., and is unalterable at 204°, but decomposes at 260°, without melting (Johnston). — The yellow is only partially soluble in *nitric acid* (Büchner). On heating it with 8 parts of nitric acid and evaporating the solution to a syrup, a bitter substance separates out, whilst the solution contains oxalic acid (and malic acid) (Braconnot). Gamboge-yellow yields with strong nitric acid crystals somewhat resembling those of mangostin (p. 330) (Schmid, *Ann. Pharm.* 93, 87). — It dissolves in *oil of vitriol* with red colour, and is precipitated in an altered state by water (Büchner). — Gamboge-yellow suspended in water is decolorised by chlorine: on evaporating the product to dryness, and treating the residue with boiling water, a pale-yellow chlorinated substance, insoluble in water, is obtained (Braconnot).

*Combinations.* Gamboge-yellow is insoluble in *water*. It combines with bases, forming Johnston's *gambodiates*.

*Ammonia-salt.* — Gamboge-yellow absorbs ammonia-gas, and afterwards dissolves slightly in water, and evolves ammonia when treated with potash (Unverdorben). It dissolves slowly in warm aqueous ammonia, with deep hyacinth-red colour, and is precipitated therefrom by carbonate of ammonia or potash (Büchner). On evaporation there remains a brittle ammoniacal residue of the colour of gamboge-yellow, insoluble in water (Johnston).

*Potash-compound.* — The yellow does not dissolve in strong caustic potash, even on warming, but easily in potash diluted with 8 parts of water, forming a dark-red solution. It expels carbonic acid when boiled with alkaline carbonates. Strong caustic potash, or its carbonate throws down a flocculent or gelatinous precipitate, according to the strength of the solution. The compound freed from admixed carbonate of potash by dissolving it in absolute alcohol, is plaster-like and coherent, neutral, easily soluble in water and in absolute alcohol, forming dark-brown solutions (Büchner).

*Soda-compound.* — Precipitated from the strong aqueous potash-compound by a saturated solution of chloride of sodium in the form of

a jelly, or from a more concentrated solution as a coherent mass, which resembles the potash-compound, but exhibits a brassy metallic lustre, and is somewhat less easily soluble in water (Büchner).

The gambodiates of the *alkaline earths* and *heavy metals* are yellow powders, insoluble in water and slightly soluble in alcohol. After drying they are not decomposed at 204°, but emit at that temperature the odour of the acid (Johnston).

*Baryta-salt.* — The cold aqueous ammonia-salt is precipitated by chloride of barium, and the precipitate is washed so long as the filtrate yields a precipitate with nitrate of silver. — Bulky, dark brick-red flocks, slightly soluble in hot water, and almost as freely in absolute alcohol: from the latter solution oil of vitriol throws down the compound of gamboge-yellow with baryta, free from sulphuric acid, but after dilution with water, it precipitates this compound together with sulphate of baryta. — It contains 65·15 p. c. C., 6·48 H., 18·06 O., and 10·31 BaO., corresponding to the formula $4C^{60}H^{35}O^{12},3BaO$. (Büchner).

*Strontia-salt.* Obtained by adding ammonia and the alcoholic solution of gamboge-yellow to an alcoholic solution of nitrate of strontia. The yellow precipitate, dried at 100°, contains 9·88 p. c. SrO. $(3C^{40}H^{24}O^8,2SrO = 9·56$ p. c. SrO) (Johnston).

The *magnesia-salt* contains 4·6 p. c. MgO., the brownish-yellow *zinc-salt* 11·10 p. c. ZnO $(C^{40}H^{24}O^8,ZnO = 10·95$ p. c. ZnO) (Johnston). — The ammonia-salt forms a fine yellow precipitate with *protochloride of tin* (Büchner); the potash-salt, a brown precipitate with *protosulphate of iron* (Pelletier).

*Lead-salts.* — The ammonia-salt precipitates neutral acetate of lead of a yellowish-red, and the basic acetate of an orange colour (Büchner). — *a.* Neutral acetate of lead containing ammonia throws down from the ammoniacal solution, a yellow powder containing 49·23 p. c. oxide of lead $(C^{40}H^{24}O^8,3PbO = 49·4$ p. c. PbO) (Johnston). — *b.* The precipitate thrown down by neutral acetate of lead from the cold aqueous ammonia-salt in presence of a slight excess of ammonia, is reddish and gelatinous. When precipitated boiling, it is flocculent, easier to wash, and triturable to a light brick-red powder after drying. It is insoluble in water and weak alcohol, but slightly soluble in absolute alcohol, forming a solution from which oil of vitriol throws down nothing at first, but after addition of water, a mixture of sulphate of lead and the lead-compound of gamboge-yellow. — It contains, on the average, 46·24 p. c. C., 4·62 H., 14·66 O., and 34·48 PbO, corresponding to the formula $2C^{60}H^{35}O^{12},5PbO$ (Büchner). — *c.* Alcoholic neutral acetate of lead throws down from the alcoholic solution of gamboge-yellow, a yellow powder, containing, at 100° to 188°, 19·47 p. c. PbO $(3C^{40}H^{24}O^8,2PbO = 18·54$ p. c. PbO) (Johnston). The precipitate is insoluble in water, sparingly soluble in alcohol, easily in ether, and contains 14·96 p. c. PbO (Unverdorben). $(2C^{40}H^{24}O,PbO = 14·58$ p. c. PbO). — *d.* On decomposing the precipitate *a* with acetic acid, a yellow powder containing 14·78 p. c. PbO remains undissolved. The same salt with 13·88 p. c. PbO is thrown down by ammonia from the liquid filtered from *c*, which probably still contains a large quantity of resin (Johnston).

*Copper-salt.* — The ammonia-salt forms a green precipitate with sulphate of copper (Büchner). Unverdorben obtained a brown-red compound, containing 4·58 p. c. CuO, soluble in ether: Johnston describes brown yellow precipitates with 18·9, 14·66, and 10·62 p. c. CuO.

*Silver-salt.* — a. Alcoholic nitrate of silver throws down from the alcoholic solution of gamboge-yellow, on addition of ammonia, a yellow precipitate, which turns dark-green in the air, and contains, on the average, 15·66 p. c. AgO (Johnston). — b. On gradually adding the aqueous ammonia-salt to aqueous ammoniacal nitrate of silver, and stirring constantly, a yellow precipitate is produced which dissolves in more ammonia, is again precipitated by the silver-salt, and unites to brown flocks on standing. After drying at 121° till it is no longer soft it contains, 9·71 p. c. AgO (Johnston). — c. Büchner, by precipitating the ammonia-salt containing a slight excess of ammonia with nitrate of silver, obtained, in the cold, a dirty yellow, somewhat slimy precipitate, which became flocculent and easier to wash when boiled. — Pale brownish-yellow powder, soluble in ammonia (Büchner).

|  |  | *According to Johnston.* |  |  | Johnston. a. |  | Büchner. c. |
|---|---|---|---|---|---|---|---|
| 80 C | 480 | ........ | 62·17 | ........ | 60·37 | ........ | 57·94 |
| 48 H | 48 | ........ | 6·22 | ........ | 6·03 | ........ | 5·74 |
| 16 O | 128 | ........ | 16·58 | ........ | 17·72 | ........ | 17·59 |
| AgO | 116 | ........ | 15·03 | ........ | 15·88 | ........ | 18·73 |
| 2C$^{40}$H$^{24}$O$^8$,AgO.... | 772 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

According to Büchner, C$^{60}$H$^{35}$O$^{12}$,AgO.

Gamboge-yellow dissolves easily in *alcohol* and *ether.*

17. GUM-LAC. — Exudes from the twigs of *Aleurites laccifera, Croton aromaticus, Butea frondosa, Ficus religiosa,* and *Zizyphus Jujuba* in India, after being punctured by *Coccus Lacca.* The *stick-lac (Lacca in ramulis)* adhering to the twigs, when removed and freed from the greater part of the colouring matter by boiling with water containing soda, yields *grain-lac (Lacca in granis),* from which *shellac* is obtained by melting and straining. — Stick-lac boiled with water and precipitated with alum yields *lac dye.* Stick-lac is dark-brown; grain-lac and shellac are yellowish-brown, orange, or black; all the varieties are translucent, hard, and of a conchoïdal, shining fracture.

Stick-lac contains resin, laccin, and colouring matter (Funke, *N. Tr.* 18), and according to Hatchett, also wax and gluten. The impurities mixed with stick-lac contain sulphide of arsenic (Büchner, *Ann. Pharm.* 59, 96). According to Unverdorben, lac colours water reddish-brown, whereupon sulphuric acid throws down a red-brown pulverulent precipitate.

According to John (*Chem. Schriften,* 5, 1) grain-lac contains two easily soluble resins and an insoluble resin (laccin), wax, colouring matter, bitter principle, ash, and impurities. Unverdorben [see his complete analyses (*Pogg.* 14, 119)] distinguishes five different resins in grain-lac. Nees v. Esenbeck & Marquart (*Ann. Pharm.* 13, 286) found a substance resembling carmine, which was extracted by water, besides wax, laccin, and two resins, one of which was soluble in ether.

Shellac (which, according to Brisson, is of sp. gr. 1·139) contains two resins and wax, but no laccin; a spurious shellac contained laccin, three resins, wax, and traces of laccic acid (Nees v. Esenbeck & Marquart). — Shellac dissolves easily in aqueous hydrochloric acid, acetic acid, potash, soda, and borax, but not in ammonia (Hatchett). Powdered lac, when digested with a little strong ammonia in closed vessels, swells up to a jelly which dissolves in water, with the exception of the wax and impurities. Cold aqueous potash dissolves lac easily : the solution is not precipitated by excess of potash. Strong aqueous carbonate of potash dissolves only a little colouring matter, and forms a fluid compound of resin and potash, which, after washing with cold water, dissolves easily in boiling water. The solution remains clear on cooling, or when too much carbonate is present, solidifies to a jelly : it is precipitated in coherent flocks by acids (Berzelius, *Pogg.* 10, 255 ; 12, 426). — Lac dissolves with moderate facility in wood-spirit, and is precipitated from the solution by water. It is perfectly soluble in fusel-oil and valerianic aldehyde, moderately soluble in valerianic acid, and slightly in valerate of amyl (Trautwein). It dissolves partially in cold creosote (Reichenbach), in more than 100 parts of boiling rock-oil (Saussure), and but slightly in benzene, though benzene mixes with the saturated solution in wood-spirit or alcohol (Mansfield). The different kinds of commercial lac behave in various ways with acetone. Bleached shellac dissolves in $1\frac{1}{2}$ parts of acetone, forming a thick oily varnish ; other kinds dissolve only in $3\frac{1}{2}$ parts, and others not at all in acetone (Wiederhold, *Polyt. Notizbl.* 19, 214). Shellac does not dissolve completely in melted tallow (Nicholson), and not perceptibly in castor oil (Stickel).

*Laccin* remains behind as a brittle, transparent, yellowish-brown mass when grain-lac is treated with alcohol, water, and hot alcohol in succession : it is purified by levigation (John). According to Büchner, it is to be regarded as a mixture of resin and wax. — When acted upon by nitric acid, it yields oxalic acid and tallow. It dissolves completely in caustic potash, and is not precipitated by sal-ammoniac, but hydrochloric acid throws down from the solution a sticky resin, soluble in alcohol and ether. Laccin is insoluble in ammonia-water, and in cold and boiling alcohol, ether, and volatile and fat oils, but dissolves in glacial acetic acid and in warm alcohol containing a little sulphuric or hydrochloric acid (Unverdorben), excepting 5 p. c. of wax (Nees v. Esenbeck & Marquart). — The *laccic acid* of Pearson (*Phil. Trans.* 1794, 383) and John crystallises in needles. It remains in solution when an alcoholic solution of stick-lac is precipitated by water, and is obtained by evaporating the filtrate and exhausting the residue with ether. It forms deliquescent acid crystals, which give white precipitates with ferric salts and with the salts of lead and mercury, and yield with the alkalis, lime and baryta, deliquescent salts soluble in alcohol (John).

The *bleaching of shellac* on the large scale is effected by chlorine or its compounds, but granulated bone-charcoal answers the purpose better (Elsner, *J. pr. Chem.* 35, 374), and especially bone-black purified by means of hydrochloric acid and not subsequently dried (Kr.). A perfectly white shellac, having a silky lustre and completely soluble in alcohol, is obtained by the following process :—25 parts of shellac are dissolved in 600 parts of water with the help of 10 parts of soda. The solution is mixed with dilute hypochlorite of soda prepared from 30 parts of chloride of lime, and then with hydrochloric acid so long

as the precipitate dissolves. It is then exposed to the sun for a day or two, filtered, mixed with sulphite of soda, and precipitated by hydrochloric acid (Sauerwein, *Hannov. Gewerbebl.* 1862, July—Aug.; *Chem. Centr.* 1863, 89).

18. ICICA RESIN. — From Cayenne. Yellowish-white pieces or transparent granules having an agreeable odour, which is emitted when the resin is warmed or powdered. It is friable, crunches between the teeth, and has a faint taste. When boiled with water it yields no volatile product and does not dissolve. It requires for complete solution 55 parts of cold, and 15 parts of boiling alcohol of 36°, and $3\frac{1}{4}$ parts of cold oil of turpentine. — It consists of three neutral resins, brean, icican, and colophan, which are all insoluble in alkalis and do not precipitate lead- or silver-salts.

*Preparation of the three resins.* Powdered icica-resin is dissolved in boiling alcohol, and the solution is filtered hot and allowed to cool, whereupon the brean crystallises. The mother-liquor, when concentrated, yields first impure brean and afterwards icican, whilst the colophan, which is much more soluble, remains in solution.

a. *Brean.* — White, pearly, stellate groups of needles, melting at about 157° and cooling to a viscid elastic mass, which again becomes solid at 105°. Tasteless. Neutral.

|  |  | at 120° |  |  |  | Scribe. mean. |
|---|---|---|---|---|---|---|
| 80 C | ............... | 480 | ........ | 84·06 | ........ | 83·92 |
| 67 H | ............... | 67 | ........ | 11·73 | ........ | 11·82 |
| 3 O | ............... | 24 | ........ | 4·21 | ........ | 4·26 |
| $C^{80}H^{64},3HO$ | .... | 571 | ........ | 100·00 | ........ | 100·00 |

Brean *burns* with a smoky flame. — When submitted to *dry distillation*, it melts, turns yellow and brown, gives off volatile oil, and a yellow amorphous sublimate, leaving charcoal. — With hot *nitric acid* it evolves red fumes and is converted into a yellow mass, which dissolves partially in the acid and is precipitated from the solution by water. — It dissolves in cold *oil of vitriol* with red colour.

Brean is insoluble in *water* and in *alkalis;* it dissolves in 100 parts of cold *alcohol*, and in 4·4 parts of *ether* (Scribe).

b. *Icican.* — Resembles brean in appearance and melting-point, and in its behaviour on dry distillation and towards acids and alkalis, but dissolves in 50 parts of cold alcohol.

|  |  | at 120° |  |  |  | Scribe. mean. |
|---|---|---|---|---|---|---|
| 160 C | ............... | 960 | ........ | 82·12 | ........ | 82·01 |
| 137 H | ............... | 137 | ........ | 11·72 | ........ | 11·64 |
| 9 O | ............... | 72 | ........ | 6·16 | ........ | 6·35 |
| $2C^{80}H^{64},9HO$ | .... | 1169 | ........ | 100·00 | ........ | 100·00 |

c. *Colophan.* — Yellow amorphous mass, melting below 100°, and having a very slight acid reaction in alcoholic solution. It is insoluble in alkalis, but very easily soluble in alcohol. It contains 77·93 p. c. C.,

10·69 H., and 11·47 O. (Scribe, *Compt. rend.* 19, 129 ; *N, Ann. Chim. Phys.* 13, 166).

19. LABDANUM or LADANUM. — A sticky, afterwards drying substance covering the leaves and branches of *Cistus creticus.* Blackbrown, soft, of sp. gr. 1·186 (Brisson). Has an agreeable odour and a bitter taste. According to Guibourt, it contains 86 p. c. of resin and volatile oil and 7 p. c. of wax, together with substances soluble in water, ash, and impurities ; according to Pelletier (*Bull. Pharm.* 4, 503) 20 p. c. of resin, 1·9 of wax, 3·6 of gum, 1·9 of volatile oil, malic acid, malate of lime, and 72 p. c. of sand containing iron.

Labdanum dissolves to the extent of ¼th at most when digested with cold alcohol of sp. gr. 0·83, forming a brown solution. On evaporating the solution, the dissolved portion is left as a dark-brown transparent mass, which gives up bitter substances and colouring matter to water. When, therefore, labdanum is boiled repeatedly with water, the residue exhausted with alcohol, and the tincture evaporated in thin layers at 100°, a purer resin is obtained, which gives up a little bitter substance to water, without altering in composition. It contains, on the average, 73·20 p. c. C., 10·01 H., and 17·79 O., corresponding to the formula $C^{40}H^{33}O^7$ (Johnston, *Phil. Trans.* 1840, 344). — Labdanum does not yield umbelliferone by dry distillation (Sommer).

20. RESIN OF LAËTIA RESINOSA.—Small, yellowish-white, transparent, brittle granules, having a conchoïdal fracture and smelling slightly aromatic. When distilled with water, it yields a little volatile oil, without giving up any thing to the residual water. When heated it melts, puffs up, and burns with a bright smoky flame, leaving a bituminous charcoal. It dissolves completely in boiling alcohol and is partly deposited from the solution on cooling (Macaire-Princep, *Bibl. univ.* 45, 431).

21. MASOPIN. A crystallisable resin forming a constituent of the sap of the Dschilte, a Mexican tree. The dried sap, imported in cylindrical masses, remains, when powdered and boiled with water, as a tough elastic mass, from which absolute alcohol extracts the masopin, leaving caoutchouc. The masopin is precipitated from the alcoholic solution by water, and may be obtained from ether in white silky needles, frequently arranged in tufts. The crystals melt at 155° and solidify, on cooling, to a glassy mass, having a conchoïdal fracture and melting at 69° to 70°. It is tasteless and inodorous, but has an agreeable smell when heated.

| | Crystals. | | | | Genth. mean. |
|---|---|---|---|---|---|
| 44 C | 264 | | 83·54 | | 83·46 |
| 36 H | 36 | | 11·39 | | 11·48 |
| 2 O | 16 | | 5·07 | | 5·06 |
| $C^{44}H^{36}O^2$ | 316 | | 100·00 | | 100·00 |

Masopin yields by dry distillation (1) a brown oil smelling of ginger, which becomes wine-yellow and limpid when rectified over lime, and contains 88·02 p. c. C., and 11·49 H. ; (2) an acid, which may be extracted from the crude oil by ammonia, and is precipitated from the ammoniacal solution in pearly laminæ by hydrochloric acid. When

combined with lime and precipitated by hydrochloric acid, it forms delicate dazzling white needles. Its silver-salt is white, smells of cinnamic acid when burnt, and contains 45·49 p. c. AgO. — Nitric acid attacks masopin violently at first, and when long boiled with it, dissolves it to a clear liquid, which leaves on evaporation a tough amorphous mass, soluble in water with wine-yellow colour. The silver-salt of this acid contains 45·46 p. c. AgO., 30·35 C., and 3·37 H. (Genth, *Ann. Pharm.* 46, 124).

22. MASTIC. — From *Pistacia Lentiscus.* Yellowish translucent tears, of sp. gr. 1·04 (Pfaff), 1·074 (Brisson), 1·07 (Schrötter). Has a glassy and transparent fracture, softens between the teeth, melts at 100° according to Johnston, softens at 80° according to Schrötter, and begins to froth up and decompose at 105° to 120°. The alcoholic solution, but not the aqueous decoction, reddens litmus (Bouillon-Lagrange & Vogel). By dry distillation it yields tar and acetic acid (Schrötter); no umbelliferone (Sommer): it yields at first, acid water, and when more strongly heated, a pale-yellow oil, limpid at first and afterwards thick, whilst a black residue, insoluble in alcohol, remains behind (Johnston). Mastic dissolves in nitric acid with decomposition, forming camphretic acid (Schwanert): it dissolves also in cold oil of vitriol, from which it is precipitated by water. It absorbs a little ammonia-gas and dissolves in aqueous alkalis. See below. It is soluble in alcohol, with the exception of the beta-resin; easily and abundantly soluble in acetone according to Wiederhold, and according to Mansfield freely soluble in benzene. It dissolves in fatty and volatile oils; in cold creosote (Reichenbach); in warm rock-oil, leaving an opaque white residue; and, according to Stickel, slightly in castor oil.

Mastic consists of a little volatile oil, a soluble acid resin, and a non-acid insoluble resin. — Picked mastic, analysed as a whole, contained 78·91 p. c. C., 10·42 H., and 10·67 O. (Schrötter, *Pogg.* 59, 68).

*Alpha-resin of Mastic.* — 1. When a cold alcoholic solution of mastic is evaporated, and the pale-yellow residue, which is fusible at 100°, is kept at a temperature of 176° for 18 hours, it has the composition *a*. — It still contains an admixture of beta-resin, which may be precipitated, in great part, by diluting the solution with a large quantity of alcohol: the resin thus purified has the composition *b*, after being heated to 126° for 18 hours, and the composition *c* after heating to 176°. — The resin heated to 176°, however, evolves white vapours, loses its odour, and when treated with alcohol, leaves a large quantity of the reddish resin *d* behind, whilst *e* is dissolved. *d* is deposited from a solution in boiling alcohol as a yellow powder: *e* is a transparent reddish-yellow mass.

2. Commercial mastic boiled for some hours with water becomes white, opaque, and less fusible, probably from loss of volatile oil; and the residue dissolves in alcohol more slowly than before. The alcoholic solution is evaporated; the residue is boiled for some time with water to expel adhering alcohol, and afterwards heated to 100° for 48 hours, whereby it becomes soft without quite melting. The opaque, pale-yellow resin thus obtained, and also the melted fine reddish-yellow, transparent mass formed by further heating to 115°, exhibit the composition *f*, and are almost entirely soluble in alcohol,

Analyses and formulæ according to Johnston.

|  | a. | b. | c. | d. | e. | f. |
|---|---|---|---|---|---|---|
|  | $C^{40}H^{32}O^4$ | $C^{40}H^{31}O^4$ | $C^{40}H^{30}O^4$ |  | $C^{40}H^{33}O^3$ | $C^{40}H^{31}O^4$ |
| C .... | 77·32 ........ | 78·35 ........ | 78·71 ........ | 77·76 ........ | 79·42 ........ | 78·19 |
| H .... | 10·40 ........ | 10·15 ........ | 10·22 ........ | 10·12 ........ | 10·88 ........ | 10·33 |
| O .... | 12·28 ........ | 11·50 ........ | 11·07 ........ | 12·12 ........ | 9·70 ........ | 11·48 |
|  | 100·00 ........ | 100·00 ........ | 100·00 ........ | 100·00 ........ | 100·00 ........ | 100·00 |

3. When the alpha-resin is melted in a retort for 24 hours, the temperature being allowed to rise at last to 132°, water and a small quantity of a crystallisable acid pass over. If the operation be suspended as soon as a pale-yellow liquid makes its appearance in the neck of the retort, and the red residue be then boiled with alcohol, it is resolved into a dark-yellow insoluble powder $g$ (which may be removed from the retort by means of boiling water, and is not fusible at 132°), a pale-yellow resin $h$, which is deposited from the alcoholic solution on cooling, and a reddish-yellow transparent resin $i$, which remains in solution. Johnston gives for $g$ the formula $C^{40}H^{30}O^5$ or $C^{40}H^{31}O^5$, and for $i$ the formula $C^{40}H^{32}O^3$; on prolonged heating, therefore, the alpha-resin $C^{40}H^{31}O^4$ breaks up into a resin with 3 atoms and a resin with 5 atoms of oxygen (Johnston).

Analyses by Johnston.

|  | g. | h. | i. |
|---|---|---|---|
| C ........ | 76·00 ........ | 78·14 ........ | 76·94 |
| H ........ | 9·86 ........ | 9·74 ........ | 10·35 |
| O ........ | 14·14 ........ | 12·12 ........ | 12·71 |
|  | 100·00 ........ | 100·00 ........ | 100·00 |

*Lead-salts of the alpha-resin.* — a. *Semi-acid.* When an alcoholic solution of the alpha-resin is precipitated by alcoholic neutral acetate of lead, and the solution is filtered from the white precipitate $c$, and cautiously mixed with ammonia, a further white precipitate is thrown down, a portion of which ($a$) remains undissolved on boiling with alcohol, whilst the rest ($c$) is deposited from the alcohol on cooling. — b. *Mono-acid.* When the above precipitate is boiled with alcohol after drying (not in a moist state) $b$ remains undissolved. — c. *Sesqui-salt.* White precipitate, turning yellow at 100°, and melting to a yellow mass, without decomposition, at 177°.

Analyses and formulæ according to Johnston.
at 149°.

|  | a. | b. | c. |
|---|---|---|---|
|  | $C^{40}H^{31}O^4,2PbO$ | $C^{40}H^{31}O^4,PbO$ | $3C^{40}H^{31}O^4,2PbO$ |
| C ........ | 45·55 ........ | 57·64 ........ | 64·64 |
| H ........ | 5·70 ........ | 7·37 ........ | 8·45 |
| O ........ | 7·39 ........ | 8·66 ........ | 8·66 |
| PbO ........ | 41·36 ........ | 26·33 ........ | 18·25 |
|  | 100·00 ........ | 100·00 ........ | 100·00 |

*Silver-salt of the alpha-resin.* — On mixing the alcoholic resin with an alcoholic ammoniacal solution of nitrate of silver, a white precipitate is produced, which, when washed with cold alcohol and dried at 149°, has the composition $a$. — If this precipitate be dissolved in boiling alcohol, the slightly coloured solution deposits, on cooling, the precipitate $b$, which sticks together in a dark mass at 149° and begins to

melt at 177°. — The solution, filtered from $a$ and mixed with more nitrate of silver, throws down $c$. These salts are represented by the formula $2C^{40}H^{30}O^3,AgO$, or $2C^{40}H^{31}O^4,AgO$ (Johnston).

Analyses by Johnston (at 121° to 149°).

|       |          |          |          |
|-------|----------|----------|----------|
| C     | 63·00    | 67·25    | 65·21    |
| H     | 8·30     | 8·64     | 8·53     |
| O     | 9·44     | 7·16     | 9·76     |
| AgO   | 19·26    | 16·95    | 16·50    |
|       | 100·00   | 100·00   | 100·00   |

*Beta-resin or difficultly soluble resin of mastic. Masticin.* — Observed by Neumann (*Chymie*, 2, 3, 11) and Matthews (*Nicholson's Journ.* 10, 247): it forms, according to the former $\frac{1}{12}$th, according to the latter $\frac{1}{6}$th of mastic. — It remains behind, when mastic is dissolved in alcohol, as a white, translucent, tough residue, which may be drawn out into long threads. On boiling with water, it becomes harder and less elastic, but recovers its elasticity after drying at 149°. — When heated it swells up and evolves an odour of rock-oil: the resulting porous mass, after cooling, is brittle and richer in oxygen than before (Johnston). When burnt it smells like mastic, not like caoutchouc. — It is not perceptibly soluble in boiling alcohol, but more easily soluble in presence of the alpha-resin and also after being dried, powdered, and kept. It dissolves in ether and oil of turpentine, but not in caustic potash (Johnston, *Phil. Trans.* 1839, 132). — Kunde (*Berl. Jahrb.* 1795, 142); Funke (*A. Tr.* 18, 2, 150); Brande (*Berl. Jahrb.* 1808, 110); Bonastre (*J. Pharm.* 8, 575).

| Calculation according to Johnston. |     |        | Johnston. |
|------------------------------------|-----|--------|-----------|
| 40 C                    | 240  | 83·63  | 82·61     |
| 31 H                    | 31   | 10·80  | 11·01     |
| 2 O                     | 16   | 5·57   | 6·38      |
| $C^{40}H^{31}O^2$       | 287  | 100·00 | 100·00    |

23. MYRRH. — From *Balsamodendron Myrrha.* Yellow, brown, or reddish, with white flocks; translucent, brittle. Has an agreeable odour and a somewhat acrid, bitter taste. Myrrh rich in oil has a neutral reaction; that poor in oil is acid (Bley & Diesel). Sp. gr. 1·12 to 1·18 (Ruickholdt). It does not melt when heated, and takes fire with difficulty. When submitted to dry distillation, it does not yield umbelliferone (Sommer). When melted with hydrate of potash, it yields an acid resembling that obtained from guaiacum (Hlasiwetz & Barth, *Zeitschr. Ch. Pharm.* 7, 285). When treated with strong nitric acid, it assumes a black-brown colour, and colours the acid a dirty violet. Blotting-paper moistened with tincture of myrrh is coloured a permanent bluish-red by fuming nitric acid (Martiny; Ruickholdt). — Myrrh distilled with water yields a volatile oil (xiv, 413) and water having an acid reaction, due to the presence of formic acid (Bley & Diesel); at the same time a white resinous sublimate condenses in the upper part of the retort, and the myrrh dissolves almost completely (Ruickholdt). Water which has been shaken with powdered myrrh precipitates lead-salts (Bley & Diesel). Myrrh forms with alcohol a pale golden-yellow tincture, leaving a white residue (Bley & Diesel, *N. Br. Arch.* 43, 304).

Myrrh contains oil, resin (myrrhin), which, according to Brandes, is decomposible by ether, gum, and 3 p. c. of ash, consisting chiefly of carbonate of lime and magnesia. The portion soluble in water contains a gum precipitable by neutral acetate of lead and a second gum precipitable by the basic acetate (Hekemeijer, *Kopp's Jahresber.* 1858, 482. — Pelletier, *Bull. Pharm.* 4, 54; Brandes, *Taschenb.* 1819, 51).

The red-brown, brittle, neutral resin, melting at 90—95°, obtained by evaporating the alcoholic tincture, is Ruickholdt's *myrrhin*. When heated it evolves white vapours smelling of myrrh, takes fire, and burns. It assumes a yellow colour (? Kr.) in strong nitric acid, dissolves partially in boiling caustic potash, completely in acetic acid and in ether, and incompletely in alcohol. Its solution in alcohol is rendered milky by water. It contains, on the average, 71·82 p. c. C., 8·15 H., and 20·03 O., corresponding, according to Ruickholdt, to the formula $C^{48}H^{32}O^{10}$. When melted and heated to 168° for some time, it froths up, from evolution of acid water. The transparent red-brown residue, Ruickholdt's *myrrhic acid*, is acid, nearly insoluble in caustic potash but soluble in alcohol and ether, with the exception of a few flocks: it contains, on the average, 74·79 p. c. C., 8·00 H., and 17·21 O., corresponding to the formula $C^{48}H^{32}O^{8}$ (Ruickholdt, *N. Br. Arch.* 41, 1). See also Heldt (*Ann. Pharm.* 63, 59).

The portion of myrrh insoluble in water, but soluble in strong alcohol, is nearly insoluble in aqueous carbonate of soda, easily soluble in ether and chloroform, and to the extent of one-half in bisulphide of carbon. The portion soluble in bisulphide of carbon assumes a violet colour when heated with nitric acid (Hager, *Pharm. Centralhalle*, 1865, 58; *Anal. Zeitschr.* 3, 483).

Tincture of myrrh kept for three years was found to have deposited pale-yellow, six-sided prisms, having an acid reaction, fusible, inflammable, soluble in hot alcohol, ether, and oils, also in caustic potash, and precipitable from the last solution by acids (Landerer, *Repert.* 68, 362).

Planche (*J. Pharm.* 26, 500; *Ann. Pharm.* 37, 121) distinguishes as *myrrhoïd* a gum-resin of unknown origin, closely resembling myrrh. It forms irregular warty or striated tears, partly somewhat opaque and covered with a grey powder, and partly brown-red, transparent, of conchoïdal fracture, and less wrinkled. After removing the adhering myrrh-powder and washing with alcohol, it is inodorous. Has a bitter and peppery taste. — When triturated with water, it forms an opaque mud, or with more water a nearly clear, slightly coloured solution, from which resin is deposited in the form of a yellow oil, together with light flocks of bassorin. Alcohol throws down gum from the solution, whilst *myrrhoïdin* remains in solution. — The resin dissolves in alcohol, from which it is precipitated in oily drops by water, but is insoluble in ether. — Myrrhoïdin is yellow, turpentine-like, highly elastic, neutral, and has a persistent bitter and acrid taste; it produces shining grease-spots on paper. When heated it melts without emitting a resinous odour, and carbonises without taking fire. It dissolves easily in cold water and completely in ammonia and caustic potash: the saturated solution turns green with nitric acid. — The alcoholic solution does not precipitate salts of lead, protoxide of tin, copper, or silver, but yields a slight precipitate with protosulphate of iron. — Myrrhoïdin dissolves easily in alcohol, ether, and oil of turpentine, but not in olive oil. It produces with tannic acid a white preci-

pitate, insoluble in excess of alcohol. See also Martiny (*Jahrb. pr. Pharm.* 10, 25).

Concerning *Myrrha nova*, see Bonastre (*J. Pharm.* 15, 281; *N. Tr.* 20, 2, 188).

24. OLIBANUM. *Frankincense. Thus.* — The Indian variety is obtained from *Boswellia serrata*, the Arabian from *Amyris Kataf.* Yellowish, translucent, brittle, covered with a mealy powder, and having a dull splintery fracture. Sp. gr. 1·221. Becomes tough between the teeth; has a balsamic odour and an acrid, bitter taste. Its alcoholic solution reddens litmus. — When distilled with water it yields an oil. Melts imperfectly, emitting an agreeable odour. When submitted to dry distillation, it yields a large quantity of brown empyreumatic oil and a little acid water [no umbelliferone (Sommer)]: the residue contains carbon and ash (Braconnot). — Olibanum takes fire when heated in the air; with nitric acid it forms, according to Hatschett, an artificial bitter, according to Schwanert, camphretic acid.

Olibanum contains 5 p. c. or more [4 p. c. (Stenhouse)] of volatile oil smelling of lemons, 56 p. c. of resin, 30 of gum [agreeing in properties with gum-arabic (Hekemeijer, *Kopp's Jahresber.* 1858, 482)] and 6 of bassorin (Braconnot, *Ann. Chim.* 68, 60).

The resin of olibanum, obtained by extracting with alcohol and evaporating the solution, is red-yellow, very brittle, tasteless, softens at 100°, and melts at a higher temperature. It dissolves in oil of vitriol, forming a red solution which is precipitated white by water. When caustic potash is poured upon it and evaporated, it yields a slightly soluble residue, which forms a thick emulsion with water (Braconnot).

The olibanum of commerce is a mixture of two resins differing in appearance: *a*, consisting of round, opaque, dull and brittle pieces, which quickly become covered with an opaque layer under alcohol; and *b*, of yellow, transparent, long tears, which are softer and less brittle than *a*, and remain clear for a longer time in alcohol. On picking out the two resins, digesting them in cold alcohol for several days, decanting from gum, evaporating the solution, and heating the residue to 121° for 16 hours, the residue from *a* contains 74·15 p. c. C., 9·98 H., and 15·87 O., corresponding to the formula $C^{40}H^{32}O^6$. The residue of *b* is pale-yellow, brittle, softens at 104°, and contains 78·04 p. c. C., 10·72 H., and 11·24 O., or 2 at. O. less than *a*. In both cases gum remains undissolved (Johnston, *Phil. Trans.* 1839, 301).

25. OPOPONAX.—From *Ferula Opoponax.* — Reddish-yellow and dirty-white; of sp. gr. 1·622 (Brisson). Has a repulsive odour and a bitter acrid taste; reddens litmus. Contains 42 p. c. of resin, besides gum, caoutchouc, starch, woody fibre, malic acid, bitter principle, wax, and volatile oil. — It forms a milk with water. By dry distillation water, acetic acid, acetate of ammonia, brown empyreumatic oil [umbelliferone (Sommer)] and charcoal are obtained (Pelletier, *Ann. Chim.* 79, 90; *Bull. Pharm.* 4, 49). — It does not yield styphnic acid with nitric acid (Böttger & Will).

The *resin of opoponax* is reddish-yellow and melts at 50°. It is decomposed by warm nitric acid, with formation of a yellow mass containing artificial bitter and oxalic acid. — It dissolves in ammonia, potash, and soda, forming reddish solutions, from which it is precipi-

tated in reddish flocks by acids. It dissolves in alcohol and ether (Pelletier).

Opoponax digested with cold alcohol and ether of sp. gr. 0·83 yields a pale brown-red solution, leaving on evaporation a transparent brown resin which has a peculiar odour, melts at 100°, and when kept at that temperature for some time, is brittle after cooling. After drying for an hour or two at 100°, it contains, on the average, 63·20 p. c. C., 6·71 H., and 30·09 O., corresponding to the formula $C^{40}H^{26}O^{14}$: when it is more strongly heated, the proportion of carbon is increased about 2 per cent. (Johnston, *Phil. Trans.* 1840, 352).

26. VARNISH OF THE PASTO INDIANS (MEXICO). — Used for covering wood and calabashes, for which purpose the varnish is spread out in thin sheets and laid upon the wood. The coating, which is soft at first, hardens in the air without cracking : it is not attacked by hot water, and but slightly by alcohol and caustic potash. — The *crude varnish* is solid, not friable, of conchoïdal fracture, heavier than water, inodorous and tasteless. At a little below 100° it becomes elastic like caoutchouc, but loses its elasticity on cooling. It is combustible, dissolves without decomposition in oil of vitriol, from which it is precipitated by water. It is insoluble in alcohol, ether, and volatile and fixed oils, but swells up very much in ether and softens when heated in fatty oils.

The varnish purified from a green resin by boiling with alcohol, forms, so long as it remains moist and warm, a dirty-white, tremulous jelly, which becomes friable, hard, and brittle on cooling, and is still soft and elastic at temperatures below 100°. It contains 70·72 p. c. C., 9·70 H., and 19·58 O. — On boiling the varnish with caustic potash, it dissolves freely, forming a soap which solidifies on cooling and dissolves in more water. Acids added to the soap throw down the varnish as a shining mass, which may be drawn out in sheets, and dries up in the air to a brittle mass melting at 130°, losing thereby the remainder of its water and acetic acid, after which it dissolves in all proportions in alcohol, ether, and oil of turpentine. It contains, like the purified varnish, 70·19 p. c. C., 10·30 H., and 19·51 O. (Boussingault, *Ann. Chim. Phys.* 52, 216 ; *J. pr. Chem.* 3, 325).

27. SAGAPENUM. — From *Ferula persica?* Yellow, brown or reddish conglomerated granules, having an odour of garlic and an acrid bitter taste. Softens in the hand, but does not melt at a higher temperature. Contains, according to Brandes, volatile oil, two resins, bassorin, gum, malic acid, ash, and impurities. — It yields umbelliferone by dry distillation (Sommer), and when treated with nitric acid, forms styphnic or other acids (Böttger & Will. — Brandes, *N. Tr.* 2, 2, 97 ; Pelletier, *Bull. Pharm.* 3, 481).

The volatile oil of sagapenum is obtained by distillation with water. It is lighter than water, yellow, limpid, and has a repulsive odour of garlic. When exposed to the sun and air, the oil is converted into a transparent varnish, acquiring at the same time a smell of turpentine. Strong nitric acid, when heated with it, turns it thick and yellowish-red, with formation of oxalic acid. It assumes a dark-red colour with oil of vitriol, and dissolves in alcohol and ether (Brandes).

The alcoholic extract of sagapenum is resolved by ether into two

resins. *a.* The *resin insoluble in ether* is brown-yellow, brittle, inodorous and tasteless, and fusible when heated. It dissolves easily in warm caustic potash and in alcohol, but is insoluble in aqueous ammonia and in volatile and fat oils. — *b.* The *resin soluble in alcohol* is red-yellow, transparent, tough at first, and has a slight odour of sagapenum, and a mild, afterwards bitter taste. It melts when warmed, and dissolves with dark-red colour in oil of vitriol. It dissolves slightly in aqueous ammonia, partially only in caustic potash, easily in alcohol and ether, and very slightly in hot oil of turpentine and oil of almonds (Brandes).

Sagapenum treated with cold alcohol of sp. gr. 0·83 yields a pale-yellow solution, a considerable residue soluble in water remaining behind. The pale-yellow resin which remains on evaporating the alcoholic solution, has a strong smell of garlic, melts at 100°, and gives up to water when repeatedly boiled therewith, a substance having a bitter and onion-like taste: the residue dried at 110°, dissolved in alcohol, again evaporated, and dried at 66°, is semifluid and contains 69·06 p. c. C., 8·51 H., and 21·43 O : after being melted for some hours at 100°, it is darker, but still remains sticky, and contains 69·84 p. c. C., 8·63 H., and 21·53 O. (Johnston, *Phil. Trans.* 1840, 361).

28. SANDARAC. — From *Thuja articulata.* Pale-yellow translucent resin, brittle between the teeth. Sp. gr. 1·05 (Pfaff), 1·092 (Brisson). Moderately fusible : does not yield umbelliferone by dry distillation (Sommer). Dissolves in caustic potash. — When boiled with water it yields a bitter, slightly acid liquid : an alcoholic solution of the resin previously boiled with water reddens litmus strongly, and even on precipitating the alcoholic solution with water, but little acid is taken up by the water (Bouillon ; Lagrange & Vogel). Sandarac dissolves easily in alcohol ; according to Giese, in cold alcohol, with the exception of the sandaracin. It dissolves rapidly in cold acetone (Wiederhold), and in cold cresote (Reichenbach).

According to Unverdorben (*Schw.* 60, 82) and Johnston (*Phil. Trans,* 1839, 293) sandarac appears to contain three different resins : gamma-resin, precipitable from the alcoholic solution of sandarac by alcoholic potash, and alpha- and beta-resins, which remain in solution and are separable by alcohol of 60 p. c., in which the alpha-resin is more particularly soluble.

*Alpha-resin.* — Its alcoholic solution reddens litmus. It is very soluble in ammonia, and is precipitated, for the most part, unchanged on boiling. It dissolves in carbonate of soda on prolonged boiling, and easily in caustic potash, from which it is precipitated as a semi-fluid mass by excess of potash, and also by salts. It dissolves in alcohol, ether, and oil of turpentine, but to the extent of one-half only in rock-oil, although the two portions have the same properties in other respects (Unverdorben).

*Beta-resin.* — On extracting the alpha-resin with alcohol, the beta-resin remains behind as a semi-fluid mass which hardens when boiled with water. It has an acid reaction. Dissolves easily in ammonia, and is deposited from the solution only on complete evaporation, not on simple boiling. It is (partially) precipitable from its potash-solution by excess of potash : the oily potash-resin dissolves easily in alcohol, but is insoluble in ether. — The beta-resin is easily soluble in absolute

alcohol, ether, and oil of cummin, but insoluble in rock-oil and oil of turpentine (Unverdorben).

*Gamma-resin.* Giese's *sandaracin* (*Scher. J.* 9, 536). When the precipitate produced by alcoholic potash in an alcoholic solution of sandarac is boiled repeatedly with 84 p. c. alcohol, that liquid takes up the compound of the beta-resin with potash : the residual compound of the gamma-resin with potash is then dissolved in 60 p. c. alcohol and decomposed by hot hydrochloric acid. — White difficultly fusible powder, having a slightly acid reaction. It takes up ammonia without becoming soluble in water. Dissolves easily in caustic potash, and is precipitable as a jelly by excess of potash. Soluble in absolute and in 84 p. c. alcohol, but not in that of 60 p. c. Dissolves in ether but not in volatile oils (Unverdorben). Giese's sandaracin is precipitated from its ethereal solution in white flocks by alcohol.

This gamma-resin appears to be identical with the first two of Johnston's resins. *a.* A concentrated syrupy solution of sandarac in alcohol, when diluted with a large quantity of alcohol, deposits white resinous flocks, which after washing with alcohol and boiling with water, are inodorous and tasteless : they do not undergo alteration at 100°, but cake together at 150°, with coloration. They contain 76·32 p. c. C., 9·91 H., and 13·77 O., corresponding with the formula $C^{40}H^{31}O^5$. — *b.* Strong solution of caustic potash or lumps of the solid hydrate, added to the concentrated alcoholic solution of sandarac, produce a deposit of potash-resin (the gamma-resin of Unverdorben), whilst a second resin (alpha- and beta-resin of Unverdorben) remains in solution. The precipitate, washed with hot alcohol, decomposed by hydrochloric acid, and purified by repeated boiling with alcohol and with water, yields a grey friable resin, melting at 260°, and containing 74·17 p. c. C., 9·41 H., and 16·42 O., corresponding to the formula $C^{40}H^{30}O^6$ (Johnston).

*c.* The solution from which the potash-resin has been separated yields, when precipitated by water and hydrochloric acid, a brittle resin of a fine yellow colour, which softens at 100°, and is completely soluble in cold alcohol and cold ether. After drying for 48 hours at 93°, whereby a hydrocarbon seems to be volatilised, it contains 74·13 p. c. C., 9·82 H., and 16·05 O., corresponding with the formula $C^{40}H^{31}O^6$ (Johnston).

Concerning *Gummi Sicopira*, see Peckolt (*N. Br. Arch.* 109, 37).

29. TACAMAHAC. The *West Indian*, from *Amyris tomentosa*, is pale-brown, opaque, very brittle, of sp. gr. 1·046 (Brisson). It is easily fusible, and soluble in alkalis and in alcohol. Has an agreeable odour and aromatic taste, arising from the presence of volatile oil, which distils with water. — The *East Indian*, from *Calophyllum Inophyllum*, is yellowish-green, transparent, soft, of an agreeable odour and bitter aromatic taste. It melts easily, and dissolves completely in alcohol. According to Sommer, it does not yield umbelliferone by dry distillation.

### C. *Fossil Resins containing Oxygen.*

1. AMBER. — *Succinum. Electrum.* — Occurs as a fossil in the bed of the sea, and in alluvial deposits. Concerning its origin and occurrence

see Göppert (*Pogg.* 38, 624; *N. Br. Arch.* 11, 201. — *Berl. Acad. Ber.* 1853, 449; *Pharm. Centr.* 1853, 616). — Yellow, transparent or translucent, also white and opaque; sp. gr. 1·065 to 1·070; hard, of smooth, conchoïdal fracture; strongly negatively electric when rubbed. In hot oil it becomes so soft that it may be bent, but it is not fusible without decomposition. Inodorous and tasteless.

Pure transparent and slightly coloured pieces of amber contain, on the average (after deducting 0·19 p. c. of ash), 78·60 p. c. C., 10·19 H., 10·99 O., and 0·22 N. (Schrötter, *Pogg.* 59, 64). It contains also sulphur in the form of an organic compound, amounting at most to 0·48 p. c., so that, on submitting amber or the portion of it soluble in ether to dry distillation, hydrosulphuric acid is evolved (Bandrimont, *Compt. rend.* 58, 678). — It contains a small quantity of fragrant oil, succinic acid [the white more than the transparent, the former tasting distinctly acid when chewed (Recluz, *J. Chem. méd.* 15, 276)], a resin easily soluble in alcohol (alpha-resin), a second resin less easily soluble (beta-resin), and an insoluble resin (gamma-resin), amounting to more than 90 p. c. (Berzelius).

When powdered amber is repeatedly exhausted with warm ether, which leaves gamma-resin, and the liquid is evaporated, there remains a mass smelling of turpentine and yielding, by distillation with water, a volatile oil having an odour of peppermint and rosemary, whilst the residual water contains succinic acid and deposits a yellow mixture of two resins. The same resins may be extracted from powdered amber by warm absolute alcohol, and freed by boiling with water from volatile oil, succinic acid, and a peculiar body which prevents the crystallisation of the succinic acid. A solution of the yellow resinous mixture in boiling alcohol of sp. gr. 0·84 deposits the beta-resin as a white powder on cooling and partial evaporation, whilst the alpha-resin is obtained by the complete evaporation of the filtrate (Berzelius).

*Alpha-resin.* — Yellow and transparent; still smelling a little of volatile oil. It yields with caustic potash a pale-yellow solution precipitable by excess of potash, and from which acids throw down a white jelly. Dissolves easily in alcohol and ether (Berzelius).

*Beta-resin.* — White inodorous and tasteless powder, melting only at a high temperature, with incipient decomposition. It forms with caustic potash a colourless solution from which acids precipitate a jelly resembling hydrate of alumina, which is white and earthy when dried. The alkaline solution is precipitated by excess of caustic potash; it leaves on evaporation a white opaque mass, which when treated with water, remains for the most part undissolved. — The resin dissolves slightly in cold alcohol of sp. gr. 0·84, and yields with the boiling liquid a solution from which it is deposited on cooling, in a mass which adheres firmly to the glass; absolute alcohol and ether dissolve it more easily, and leave it as a fine powder on spontaneous evaporation. — When the mixture of alpha- and beta-resin is dissolved in aqueous potash, and the solution is evaporated, there remains a residue from which water and alcohol extract the compound of the alpha-resin, leaving that of the beta-resin undissolved (Berzelius).

*Gamma-resin.* — The gamma-resin, heated in the air, emits fumes smelling of heated fat, swells up without melting, and turns black-brown, and is then soluble in alcohol and in ether. When heated without access of air, it melts, and on cooling solidifies to a dark-brown mixture of resins, from which alcohol, ether, and rock-oil, employed in

succession, extract resins. — The gamma-resin yields by dry distillation colourless water with a trace of succinic acid, and afterwards an empyreumatic oil, leaving charcoal. — It is insoluble in hot caustic soda, but when boiled therewith till it melts, it gives off fumes and yields a colourless empyreumatic oil, leaving a residue from which cold water takes up the excess of soda containing a little resin and succinic acid, whereupon the remainder dissolves almost entirely in warm water. — The gamma-resin is insoluble in alcohol, ether, and volatile oils (Berzelius, *Pogg.* 12, 419).

When amber is exhausted with ether, the tincture evaporated, and the residue boiled with water to expel ether and volatile oil, there remains an opaque, brittle resin of agreeable odour, softening at 90°, and becoming fluid at 170°; after melting it softens only at 100°, and is transparent and harder than before. When subjected to dry distillation, it yields nearly as much succinic acid as the amber from which it is obtained. It contains, on the average, 78·49 p. c. C., 10·08 H., and 11·43 O. — The amber-resin insoluble in ether does not yield succinic acid, even after heating with sulphuric acid (x, 108) (Schrötter, *Pogg.* 59, 64).

The portion of amber insoluble in ether and alcohol (Forchhammer's *succinin*) contains 79·69 p. c. C., 10·22 H., and 10·19 O., and has therefore the same composition as sylvic acid (xvii, 318). — The soluble portion is a mixture of boloretin (p. 434) and succinin, containing 78·58 p. c. C., 10·07 H., and 11·36 O.: its solution in hot alcohol deposits, on cooling, flocks resembling boloretin (Forchhammer, *Ann. Pharm.* 41, 47).

Amber when submitted to *dry distillation*, melts, turns brown, swells up, evolves carbonic acid and combustible gas, together with water containing succinic acid, acetic acid, and empyreumatic oil (*Spiritus succini*), and yields a sublimate of succinic acid and a distillate consisting of first a thin, and afterwards a thick empyreumatic oil (xiv, 323); a residue soluble in alcohol and oils is left behind (*Colophonium succini*). — The residue when further heated, boils up strongly and yields a brown-yellow oil: the residue turns solid, carbonises, and gives off yellow vapours of chrysene (xv, 1) and succisterene (xvi, 248), together with carbonic acid, hydrocarbons, and a little water. — No umbelliferone is found amongst the products of distillation (Sommer).

Amber is violently attacked by moderately warm *nitric acid* of sp. gr. 1·34: the solution obtained by boiling for some days deposits with water a large quantity of pale-yellow flocks soluble with brown colour in ammonia, and contains camphretic acid, $C^{20}H^{14}O^{14}$ (Schwanert, *Ann. Pharm.* 128, 122). — *Oil of vitriol* digested with amber at a gentle heat forms a brown solution from which water throws down yellow flocks containing sulphur (Unverdorben). Hot oil of vitriol produces a black resin (Hatchett). — On rapidly distilling powdered amber with hydrochloric acid, there pass over, besides succinic acid, yellow laminæ, which, after washing with hot water, may be purified by repeated crystallisation from absolute alcohol. They form micaceous laminæ, lighter than water, soft, opaque, inodorous and tasteless, melting at 85° to 86°, boiling above 300°, containing 85·41 p. c. C. and 13·71 H., or equal numbers of atoms of carbon and hydrogen, and differing from chrysene (Bley & Diesel, *N. Br. Arch.* 55, 171). — When amber is boiled with excess of potash, the liquid contains succinic acid and a small quantity of resin, which dissolves partially in water after the

removal of the alkaline liquid (Berzelius). Alcoholic potash acts in a similar manner (Unverdorben, *Pogg.* 8, 407). The mixture of concentrated caustic potash and powdered amber evolves when boiled to dryness an odour of camphor, and yields a distillate of amber-camphor (Reich, *N. Br. Arch.* 51, 26).

The *amber-camphor* just mentioned is obtained by distilling powdered amber with $\frac{1}{4}$th its weight of potash and a large quantity of water, and amounts to $\frac{3}{10}$ths p. c. It resembles common camphor, has a peculiar penetrating odour, and is isomeric with borneol (xiv, 332), but acts less powerfully on polarised light, rotating a ray to the right ($[\alpha]j =$ 4·5°). Like borneol it forms with hydrochloric (xiv, 353) and stearic acids (xvii, 125) compounds from which potash separates it unaltered; it is likewise oxidised by nitric acid to a compound isomeric with common camphor. It appears to exist in amber in the form of a compound ether (Berthelot & Buignet, *Compt. rend.* 50, 606; *Ann. Pharm.* 115, 244).

Boiling *water* extracts from powdered amber a small quantity of succinic acid (Gehlen). — *Alcohol* and *ether* extract the acid, together with volatile oil and the soluble resins (Berzelius). It is nearly insoluble in *acetone* (Widerhold), quite insoluble in fusel-oil, valerianic aldehyde, valerianic acid, and valerate of amyl, but swells up in these liquids; slightly soluble in *carbolic acid* (Runge); swells up in *creosote*, and dissolves more abundantly than copal (Reichenbach). It dissolves in 20 parts of *cajeput-oil* (Draper), is insoluble in *rock-oil* (Saussure), not perceptibly soluble in *castor-oil* (Stickel); other volatile and fat oils dissolve amber either not at all or very sparingly, if it has not been altered by fusion.

2. AMBRITE. Occurs in pieces of the size of the head in the lignite of Drury and Hunu, New Zealand. Amorphous, semi-transparent, brittle, with a conchoïdal fracture and yellowish-grey colour. Sp. gr. 1·034 at 15°. Combustible. Soluble in bisulphide of carbon, leaving an amorphous white mass; insoluble in boiling alcohol, ether, oil of turpentine, benzene, and chloroform. Decomposed by melting with hydrate of potash or by boiling with nitric acid (v. Hauer). Contains, according to Maly, 76·53 p. c. C., 10·48 H., and 12·8 O., with 0·19 p. c. of ash, corresponding to the formula $C^{32}H^{26}O^4$ (v. Hauer, *Kopp's Jahresber.* 1861, 1034).

3. ANTHRACOXENE. — From Brandeisel near Schlau in Bohemia. Occurs between shale in brownish-black brittle layers, 2½ lines thick. Sp. gr. 1·181. Combustible. Melts easily, swelling up. Contains 11 p. c. of ash, the remainder consisting of 75·3 p. c. C., 6·2 H., and 18·5 O. — It dissolves partially in warm ether, leaving a black powder. On evaporating the ethereal solution, there is deposited, when the ether is reduced to one-half, a brown powder containing 81·47 p. c. C., 8·71 H., and 9·82 O.: in the unaltered state it is insoluble in alcohol, but after drying at 100°, during which it absorbs oxygen, it is partially soluble in that liquid. According to Laurentz, it is represented by the formula $C^{80}H^{81}O^7$ (Laurentz, *Wien. Acad. Ber.* 21, 271; *J. pr. Chem.* 69, 428).

4. ASPHALT. Closely related on the one hand to the fossil-resins, bitumen, and rock-oil, and on the other hand to coal, but distinguished from the latter by its fusibility and its solubility in oil of turpentine.

It either occurs in the separate state (*Erdpech*; *Judenpech*) or is obtained from earthy asphalt by boiling it with water (*Goudron*). — Black opaque lumps, of sp. gr. 1·07 to 1·17, brittle, and frequently with a pitchy lustre. The asphalt obtained by boiling the earthy substance with water is often soft, elastic, and sticky, or softens with the warmth of the hand. It burns with a smoky flame. Dissolves with black colour in oil of vitriol, generally only partially in ether, but completely in oil of turpentine, with the exception of earthy impurities. Alcohol takes up little or nothing. Caustic potash dissolves asphalt (from the Dead Sea?) according to Thorey, but not that from Dax (Völckel), nor that from Bentheim (Stromeyer. — Thorey, *Crell. Chem. J*, 6, 56). — Asphalt from Bastennes (Meyrac, *J. Phys.* 94, 128); from Mexico (Regnault, *Ann. des Mines* [3] 12, 224; Ebelmen, *Ann. des Mines*, [3] 15, 523; Bouissingault *Ann. Chim. Phys.* 73, 442); Kersten on asphalt from the island of Brazza, Dalmatia (*J. pr. Chem.* 35, 271); Stromeyer (*Leonh. u. Bronn, Jahrbuch* 1861, 189); Wetherill (*Kenngott's Jahrbuch.* 1854, 140); Hermann (*J. pr. Chem.* 73, 230).

### Analyses of Asphalt.

#### Ebelmen.

| | Regnault. | | Pont du Château. | | Boussingault. | Wetherill. | Stromeyer. |
|---|---|---|---|---|---|---|---|
| | Mexico. | Bastennes. | | Naples. | Coxitambo. | Cuba. | Bentheim. |
| C .... | 80·34 .... | 84·54 .... | 76·41 .... | 80·62 .... | 88·67 .... | 82·67 .... | 86·68 |
| H .... | 9·57 .... | 9·58 .... | 9·58 .... | 8·28 .... | 9·68 .... | 9·14 .... | 9·30 |
| N ... | .... | 1·80 .... | 2·37 .... | 1·06 .... | .... | .... | 0·66 |
| O .... | 10·09 .... | 4·08 .... | 11·64 ... | 10·04 .. | 1·65 .... | 8·19 .... | 2·82 |
| | 100·00 .... | 100·00 .... | 100·00 .... | 100·00 .... | 100·00 .... | 100·00 ... | 99·46 and 0·54 p. c ash. |

The *bitumen of Bechelbronn* in Alsace occurs mixed with sand, and is purified by boiling with water, during which the purer bitumen rises to the surface and is skimmed off. It is tough and dark-brown, and after being dissolved in ether and evaporated, contains 85·9 p. c. C., 11·25 H., and 2·85 O. When distilled with water, or when heated to 250° for some days, it yields a distillate of *petrolene:* the residue is *asphaltene*, forming a black shining mass, having a conchoïdal fracture, softening at 100°, and burning like a resin; it dissolves in ether and in volatile and fat oils, but not in alcohol. Asphaltene is obtained in a purer state by heating bitumen to 250° for 40 or 50 hours. It contains 74·23 p. c. C., 9·9 H., and 15·87 O., corresponding to the formula $C^{20}H^{16}O^3$. — Petrolene is pale-yellow, of sp. gr. 0·891, and boils at 280°. It is inflammable. Its vapour-density is 9·415 (calc. for $C^{40}H^{32} = $ 9·429). It contains 87·15 p. c. C., and 12·28 H., corresponding to the formula $C^{40}H^{32}$ (calc. 88·23 p. c. C., 11·77 H.) (Boussingault, *Ann. Chim. Phys.* 64, 145).

The brownish-yellow asphalt-oil obtained by the dry distillation of the *asphalt-stone of Neuenburg* in iron cylinders, when submitted to fractional distillation, passes over for the most part between 120° and 200°, the smaller portion distilling at 200—250°, and leaves a little dark, thick residue. Both portions have the same composition (87·46 p. c. C., 11·61 H., and 0·93 O.) but differ in specific gravity (0·817 and 0·868). They are violently attacked by nitric acid, which converts

them into resins, and are dissolved to the extent of one-half by oil of vitriol, forming red solutions. The undissolved portion, again treated with oil of vitriol and caustic potash, distils between 120° and 250°, the distillate varying in specific gravity between 0·784 and 0·867, but containing, at all the different boiling-points, an amount of carbon and hydrogen agreeing with the formula $C^6H^5$ (87·31 to 87·59 p. c. C., 12·30 to 12·69 H.) (Volckel, *Ann. Pharm.* 87, 139). See also v. Perger (*Wien. Acad. Ber.* 35, 489).

5. BERENGELITE. — Occurs in large quantities in the province of St. Juan de Berengela, 100 miles from Arica. — Dark-brown, hard mass, triturable to a yellow powder. It is insoluble in water, but dissolves abundantly in cold alcohol, which leaves it on evaporation as a transparent, red, sticky mass, becoming brittle only after some months. It dissolves easily in ether, and in a boiling dilute solution of caustic potash, from which it is precipitated by acids, but is insoluble in strong caustic potash. It is precipitated from its alcoholic solution by neutral acetate of lead. The crude earth-resin contains 71·01 p. c. C., 9·28 H., and 19·71 O. The residue left on evaporating the alcoholic solution contains, at 100°, 72·81 p. c. C., 9·37 H., and 17·82 O. (Johnston, *Phil. Mag.* 14, 89; *J. pr. Chem.* 17, 110: further *Phil. Trans.* 1840, 346).

6. BOLORETIN. Occurs in the bark and wood of fossil pines from Danish peat-bogs, and more abundantly in a grey earth found in hollow fossil pine-trunks; also in peat from Jylland, and in freshly-dropped pine-needles. The portion of amber soluble in ether contains boloretin. — It is extracted from these bodies by boiling with alcohol, from which it is deposited as a grey powder on cooling; and may be purified by repeatedly dissolving it in boiling alcohol, or by precipitating the alcoholic solution with neutral acetate of lead, whereby colouring matters are thrown down. — It forms white amorphous flocks, melting at 75°, decomposible by anhydrous phosphoric acid, with formation of empyreumatic oil. Contains

| | | |
|---|---|---|
| From pine needles...... | 73·46 p. c. C., 11·50 H., and 15·04 O. | |
| From Jylland peat: from | 74·19 p. c. C., 11·84 H., and 13·97 O. | |
| to .. | 75·50 p. c. C., 11·70 H., and 12·80 O. | |

According to Forchhammer, it is to be regarded as a hydrate of turpentine, $C^{40}H^{32} + 5HO$ (calc. 75·73 p. c. C., 11·7 H.); a part of the water is expelled when boloretin from fresh pine needles is allowed to stand for a month covered with alcohol, and afterwards boiled with water, dried, and melted, the product thus obtained containing 79·6 p. c. C., 11·01 H., and 9·39 O., and corresponding to the formula $C^{42}H^{32} + 3HO$ (calc. 80·2 p. c. C., 11·7 H.) (Forchhammer. *Ann. Pharm.* 41, 44).

The lignite of the Westerwald contains a resin soluble in ether, and a second resin resembling boroletin (Krämer, *N. Br. Arch.* 27, 73).

7. EARTH-RESIN FROM BUCARAMANGA (New Granada). — Occurs in large pieces, one of which was found to weigh 24 pounds, in an alluvial deposit yielding gold. — Pale-yellow and translucent, easily fusible, electric when rubbed, a little heavier than water. — Burns with a slightly smoky flame, leaving no residue. Does not yield succinic acid

by dry distillation. — Insoluble in alcohol. Swells up in ether, and becomes opaque. Contains 82·72 p. c. C., 10·85 H., and 6·43 O. (Boussingault, *N. Ann. Chim. Phys.* 6, 507; *J. pr. Chem.* 28, 380).

8. COPALIN. — *Highgate resin* or *Fossil Copal.* From the blue clay of Highgate-hill, London. — Yellowish-brown or dirty-grey translucent pieces, having a resinous lustre, softer than copal, harder than pine-resin. Melts easily without decomposition ; smells aromatic and resinous, especially when broken or warmed. Volatilises, according to Johnston, at a gentle heat, leaving a little charcoal and ash. Sp. gr. 1·046 (Thomson), 1·05 (Bastick). — Very easily inflammable. Dissolves in oil of vitriol, forming a dark purple solution, from which water precipitates charcoal (Bastick). According to Bastick, nitric acid converts it into fosresinic acid; according to Thomson, the acid reddens, and partly dissolves it, forming a red solution, from which it is precipitated in white bitter flocks by water. — Copalin dissolves very slightly in alcohol ; the solution is precipitated white by alcoholic neutral acetate of lead (Johnston, *Phil. Mag.* Feb. 1839, 87 ; *J. pr. Chem.* 17, 107). Insoluble, or according to Thomson (*Thoms. Ann.* 2, 9), slightly soluble in boiling caustic potash ; easily soluble in ether (Bastick, *Pharm. Journ.* 8, 339 ; *Repert.* (3) 10, 169 ; *J. Chim. méd.* 25, 383).

To this place belongs a fossil resin from the East Indies. Light honey-yellow, transparent, of waxy lustre, and having a conchoïdal fracture. Sp. gr. 1·053. Brittle. Melts easily to a clear liquid, takes fire, and burns. Dissolves for the most part in oil of vitriol, and slightly in alcohol (Kenngott, *Kenny. Jahresber.* 1850 and 1851, 147). Analysed by Duflos.

|  |  |  |  |  | Johnston. |  |  |  | Duflos. |
|---|---|---|---|---|---|---|---|---|---|
| 80 C | 480 | | 85·41 | | 84·79 | | 85·05 | | 85·73 |
| 66 H | 66 | | 11·74 | | 11·79 | | 11·48 | | 11·50 |
| 2 O | 16 | | 2·85 | | 3·42 | | 3·47 | | 2·77 |
| $C^{80}H^{66}O^2$ | 562 | | 100·00 | | 100·00 | | 100·00 | | 100·00 |

Bastick's *Fosresinic acid* is formed by treating copalin with hot nitric acid. It is a yellow amorphous powder, very acid and bitter, slightly soluble in cold, more easily in hot water, soluble also in alkalis, forming red-brown solutions, precipitable by salts of the earths and metals. It dissolves in alcohol and ether.

9. EUOSMITE. — From the lignite of Thumsenreuth in the Upper Palatinate. Brown-yellow dusty masses, or hard compact pieces, of the colour of cherry-tree wax. Brittle, with a conchoïdal fracture. Has an agreeable odour of camphor and rosemary, even after melting. Melts at 77°. Burns with a luminous flame, emitting an aromatic odour. Dissolves slightly in boiling caustic potash, and in boiling ammonia-water, which it colours yellow. Partially soluble in oil of vitriol, with separation of carbon ; boiling oil of vitriol is coloured yellowish-brown by it. — Dissolves easily in cold alcohol and ether, and remains as a glutinous mass on evaporation. Dissolves completely in hot oil of turpentine (Gümbel, *Leonhard u. Bronn, Jahrbuch,* 1864, 10). Contains 81·89 p. c. C., 11·73 H., and 6·38 O., corresponding to the formula $C^{34}H^{29}O^2$ (Wittstein).

10. FOSSIL CAOUTCHOUC. — The *English* variety is brown, translucent, of sp. gr. 0·926, soft, less tough and elastic than ordinary caout-

chouc, has an even and smooth conchoïdal fracture with somewhat fatty lustre, and a bituminous smell (Klaproth). — The *French* is black-brown, opaque, lighter than water, and very tough and elastic (O. Henry.) — Melts easily, and burns with a very smoky flame ; after melting it is very slightly elastic, and soluble in volatile oils (Klaproth). When submitted to dry distillation, it yields a yellow empyreumatic oil. — The English variety is insoluble in water and alcohol : it swells up in rock-oil and oil of turpentine without dissolving (Klaproth), *Beitr.* 3, 107). — Boiling ether or oil of turpentine extracts from English caoutchouc a yellowish-brown, sticky, bitter substance, soluble in aqueous potash ; the portion insoluble in ether or oil of turpentine (about half the caoutchouc) is grey, paper-like, and partially soluble in potash (O. Henry, *J. Chim. méd.* 1, 18).

The elastic earth-resin of Derbyshire occurs in three varieties. 1. Brown, sticky, soft, elastic mass, having a strong smell, and giving off odorous constituents at 100°. Contains 83·88 p. c. C., 13·28 H., and 2·84 O. — 2. Dark-brown, caoutchouc-like substance, harder than 1. When boiled with water, it deposits a soft, white-brown substance, which is also extracted by boiling alcohol or ether. After boiling with ether and alcohol, which dissolve 18 p. c., it contains 82·80 p. c. C., 12·58 H., and 4·62 O. — 3. Brittle pieces sometimes occurring in the soft mass, and containing 84·46 p. c. C., 12·38 H., and 3·16 O. (Johnston, *J. pr. Chem.* 14, 442 ; *Phil. Mag.* 13, 22).

11. GUYAQUILLITE. — A South American earth-resin from the neigh-bourhood of Guyaquil. Pale-yellow, opaque, soft, and easily triturable. Sp. gr. 1·092. Its alcoholic solution tastes very bitter : it yields pale-yellow prisms on evaporation. The resin melts at 70° to a viscid liquid, which becomes limpid at 100°, and remains tough and sticky on cooling. — Dissolves very slightly in water. Decomposed by nitric acid, and dissolved with red-brown colour by oil of vitriol. — Soluble in ammonia-water, and more easily in potash, forming yellow solutions precipitable by acids : the alcoholic solution is rendered darker and brown-red by ammonia. Neutral acetate of lead precipitates the alcoholic solution yellow. Nitrate of silver produces no precipitate at first : the slight precipitate thrown down after a few hours becomes more abundant on addition of ammonia, and turns brown or black. — The resin dissolves abundantly in alcohol, forming a pale-yellow solution. It contains 75·98 p. c. C., 8·18 H., and 15·84 O., correspond-ing to the formula $C^{40}H^{26}O^5$ (Johnston, *Phil. Mag.* 13, 329 ; *J. pr. Chem.* 16, 102).

## 12. Hartin.

SCHRÖTTER. *Pogg.* 59, 45.

Different from Hartite, a fossil-resin not containing oxygen.

From the lignite of Oberhart near Gloggnitz, Austria. Occurs as a deposit in the transverse fissures of lignite, and is extracted by ether.

*Purification.* 1. The hartin obtained by scraping is washed with ether so long as the liquid is coloured, and the residue, freed from

ether, is dissolved in boiling rock-oil, from which crystals are deposited on cooling. The crystals are pressed, washed with alcohol, and afterwards with ether, and dried at 200°. — 2. If the lignite is exhausted with ether in a percolator, the ether dissolves hartin through the medium of the other resins present, and deposits it in laminæ on partial evaporation.

Long white needles, of sp. gr. 1·115, without smell or taste, triturable to a powder between the fingers. Hartin crystallised from rock-oil softens at 200°, and melts at 210°; that crystallised from ether melts only at 230°, with decomposition, to a clear yellowish oil, which afterwards becomes darker, evolving a disagreeable odour, and solidifies in a waxy mass on cooling. From this mass ether takes up the changed portion, forming a dark-coloured solution, whilst unchanged hartin remains behind. — Combustible. Distils at 260° as a yellow empyrumatic oil, which solidifies to a brown-yellow crystalline mass on cooling. During the distillation, combustible gases are evolved, and a little acid liquid is also formed. By dissolving the distillate in ether and evaporating the solution, white crystals are obtained. — Hartin is completely decomposed by hot oil of vitriol, but scarcely at all by the cold liquid. — It dissolves very slightly in absolute alcohol, even at the boiling heat, but is somewhat more soluble in ether, and still more so in rock-oil.

|  |  |  |  |  | Schrötter |  |  |
|  |  |  |  |  | a. |  | b. (mean). |
| 40 C | 240 | ........ | 78·94 | ........ | 78·26 | ........ | 78·40 |
| 32 H | 32 | ........ | 10·53 | ........ | 10·92 | ........ | 10·92 |
| 4 O | 32 | ........ | 10·53 | ........ | 10·82 | ........ | 10·68 |
| $C^{40}H^{32}O^4$ | 304 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Schrötter's formulæ is $C^{20}H^{17}O^2$. *a* was prepared according to 1, *b* from lignite according to 2.

*Amorphous resin from the ethereal extract of Lignite.* — The ethereal solution from which hartin has crystallised leaves on evaporation a black asphalt-like residue, which, when dissolved in a small quantity of ether, deposits a little more hartin, and may then be separated, by treating it with absolute alcohol into alpha-resin which dissolves, and beta-resin which remains behind. The alpha-resin softens at 100°, and melts at 120°, without becoming limpid : it yields brown precipitates with neutral acetate of lead and nitrate of silver. The beta-resin softens only at 205°, and puffs up at 210°, from incipient decomposition.

| *According to Schrötter.* |  | Schrötter. a. |  | | |  | Schrötter. β. |
| 42 C | 252 | 78·51 | 78·48 | 32 C | 192 | 75·9 | 75·66 |
| 29 H | 29 | 9·05 | 9·17 | 21 H | 21 | 8·3 | 8·56 |
| 5 O | 40 | 12·44 | 12·35 | 5 O | 40 | 15·8 | 15·78 |
| $C^{40}H^{29}O^5$ | 321 | 100·00 | 100·00 | $C^{32}H^{21}O^5$ | 253 | 100·0 | 100·00 |

On *Hircin-resin*, see Piddington (*Chem. Gaz.* 1852, 216 ; *Pharm. Centr.* 1853, 28.)

13. JAULINGITE. — From Jauling in Lower Austria, occurring in lignite. Irregular lumps or thin plates of a fine hyacinth-red colour

and waxy lustre, brittle, triturable to a pale-yellow powder. Sp. gr. 1·098 to 1·111. It is combustible and easily fusible, and yields by dry distillation a brown empyreumatic oil. — Contains a portion soluble in bisulphide of carbon, of a brown-yellow colour, brittle, softening at 50°, easily soluble in ether and alcohol, but almost insoluble in caustic potash, *a.* — The remainder, which may be extracted by ether, is brown-yellow and brittle, softens at 135°, becomes tough at 160°, and dissolves in alcohol, ether, and warm caustic potash, *b* (Ragsky, *Wien. Acad. Ber.* 16, 366; *Kenng. Jahresber.* 1855, 115).

| *a.* | | Ragsky. mean. | | *b.* | | Ragsky. mean. |
|---|---|---|---|---|---|---|
| 26 C ............ | 78 | ........ 77·97 | 18 C ............ | 71·05 | ........ | 70·90 |
| 20 H ............ | 10 | ........ 10·14 | 12 H ............ | 7·89 | ........ | 7·94 |
| 3 O ............ | 12 | ........ 11·89 | 4 O ............ | 21·06 | ........ | 21·16 |
| $C^{26}H^{20}O^3$ .... | 100 | ........ 100·00 | $C^{18}H^{12}O^4$ .... | 100·00 | ........ | 100·00 |

14. IXOLYTE. — An amorphous hyacinth-red resin, occurring, together with hartite, in the fossil wood of Oberhart, near Gloggnitz: it is found more especially in the cracks of the wood, sometimes in contact with hartite, from which, however, it differs distinctly in colour and texture. It has a conchoïdal to earthy fracture and a fatty lustre, and is friable between the fingers. Sp. gr. 1·008. Softens at 76°, and is still viscid and elastic at 100° (Haidinger, *Pogg.* 56, 345).

15. KRANTZITE. — Occurs in the lignite of Lattorf, near Bernburg, in pieces of the size of the fist, containing a light-yellow or greenish translucent and inodorous resin, covered with an opaque yellowish coating. The resin has a sp. gr. of 0·968, begins to melt at 225°, but becomes fluid only at 288°, turning brown, and yields a brown oil and gases at 300—375°. It dissolves only to a small extent in alcohol and ether, swells up in volatile and fat oils, and in chloroform and bisulphide of carbon; is insoluble in alkalis, but dissolves in oil of vitriol with red-brown colour, and yields by dry distillation a brown oil free from formic and succinic acids. After being heated till it begins to melt, a portion is dissolved by alcohol, from which it is precipitated by neutral acetate of lead: the remainder is taken up by ether, forming a yellow solution. The ethereal solution leaves on evaporation an acid amorphous residue, which is friable at 0°, soft at 12°, and contains 79·25 p. c. C., 10·41 H., and 10·34 O., corresponding to the formula $C^{40}H^{30}O^4$ or $C^{40}H^{32}O^4$ (Bergmann, *J. pr. Chem.* 76, 65; abstr. *Chem. Centr.* 1859, 666).

16. MELANCHYM. — Yellowish-brown, bituminous substance, from the lignite of Zweufelsreuth, near Eger (Haidinger, *Kenng. Jahresber.* 1853, 134). By dry distillation it yields an empyreumatic oil, apparently free from succinic acid, and leaves charcoal (Rochleder).

Melanchym is resolved by treatment with warm alcohol into a residual black jelly, and a soluble portion, which is left on evaporating the solution as a brittle red-brown mass *a*, triturable to a pale-brown powder, melting above 100°, and combustible. — The black jelly, after washing with aqueous alcohol, dissolves in caustic potash, from which hydrochloric acid throws down the brown flocks *b* (Rochleder, *Ann. Pharm.* 78, 248; *Wien. Acad. Ber.* 6, 53).

| *a.* | | | Rochleder. | *b.* | | | Rochleder. |
|---|---|---|---|---|---|---|---|
| 40 C | 76·80 | ........ | 76·79 | 80 C | 67·22 | ........ | 67·14 |
| 28 H | 8·72 | ........ | 9·06 | 34 H | 4·76 | ........ | 4·79 |
| 6 O | 14·48 | ........ | 14·15 | 25 O | 28·02 | ........ | 28·07 |
| $C^{40}H^{28}O^6$ .... | 100·00 | ........ | 100·00 | $C^{80}H^{34}O^{25}$ .... | 100·00 | ........ | 100·00 |

17. MIDDLETONITE. — Round masses, occurring in thin layers in the coal-measures of Leeds. Hard, brittle, transparent, and dark-red in thin layers; red-brown by reflected light. Sp. gr. about 1·6. Inodorous and tasteless. Turns black and like coal in the air. It does not undergo alteration at 205°, melts when submitted to dry distillation, and burns like a resin on charcoal. Boiling nitric acid softens and dissolves it with decomposition. Oil of vitriol dissolves it, liberating sulphurous acid, and forming a dark-brown solution. Boiling alcohol, ether, and oil of turpentine are coloured yellow by it, but dissolve only traces. It contains 84·59 p. c. C., 8·03 H., and 7·38 O., corresponding to the formula $C^{40}H^{29}O^2$ (Johnston, *Phil. Mag*, 12, 261; *J. pr. Chem.* 13, 436).

18. PIAUZITE. — From the lignite of Piauze (Carniola). Black-brown, of fatty lustre, and imperfect conchoïdal fracture, friable between the fingers. Sp. gr. 1·22. Melts at 315°, takes fire, and burns with a brisk flame and much smoke, evolving an aromatic odour. By dry distillation it yields a yellow, acid oil. — It dissolves completely in caustic potash and in absolute alcohol, but only partially in weak alcohol and in ether (Haidinger, *Pogg.* 62, 275).

19. PYRORETIN. — A brown earth-resin from the lignite of Salesl, near Aussig, in Bohemia. Nodules from the size of a nut to that of the head, or thick plates, brittle, and easily triturable. Sp. gr. 1·05 to 1·18. Combustible. When boiled with alcohol, it leaves a residue which is quite insoluble in boiling strong caustic potash (*c*). The alcohol, on cooling, deposits the powder *a*, and when filtered therefrom and evaporated, leaves a brown resinous mass, which dissolves in ether, with the exception of some black flocks, and is recovered as a light brown brittle mass (*b*) by evaporating the solution (Stanek, *Wien. Acad. Ber.* 12, 551; *Kenng. Jahresber.* 1854, 141).

| *a.* | | | Stanek. | *b.* | | | Stanek. |
|---|---|---|---|---|---|---|---|
| 40 C | 80·00 | ........ | 80·02 | 80 C | 81·08 | ........ | 81·09 |
| 28 H | 9·33 | ........ | 9·42 | 56 H | 9·46 | ........ | 9·47 |
| 4 O | 10·67 | ........ | 10·56 | 7 O | 9·46 | ........ | 9·44 |
| $C^{40}H^{28}O^4$ .... | 100·00 | ........ | 100·00 | $C^{80}H^{56}O^7$ .... | 100·00 | ........ | 100·00 |

| *c.* | | | Stanek. |
|---|---|---|---|
| 39 C | ............ | 76·97 | 76·71 |
| 22 H | ............ | 7·24 | 7·31 |
| 6 O | ............ | 15·79 | 15·98 |
| $C^{39}H^{22}O^6$ | ............ | 100·00 | 100·00 |

20. RETINASPHALT. — A yellowish-brown body, of earthy appearance, seldom compact and shining, of sp. gr. 1·07 to 1·35. Fusible. Burns with white flame, emitting an aromatic odour. — Retinasphalt from the Saalkreise contains 91 p. c. of easily soluble resin, and 9 p. c. of an

insoluble resin resembling amber (Buchholz, *Schw.* 1, 290). That from Cape Sable contains 42·5 p. c. of easily soluble, 55 p. c. of insoluble resin, and 1·5 p. c. of oxide of iron and alumina (Troost). That from Bovey contains, according to Hatchett (*A. Gehl.* 5, 316), 55 p. c. of easily soluble, and 42 p. c. of insoluble resin; according to Johnston, 13·23 p. c. of mineral substances, 27·45 of resin soluble, and 59·23 p. c. of resin insoluble in alcohol, the last of which is Johnston's *retinic acid.* It remains, on evaporating the alcoholic solution, as a pale-brown resin, which emits a resinous odour at 100°, melts with loss of weight at 120°, and gives off bubbles of gas at 205°. It dissolves freely in ether, from which it is precipitated in great part by alcohol; and is slightly soluble in alcohol, and precipitable therefrom by water. The alcoholic solution is slightly precipitated by chloride of calcium, and more abundantly by alcoholic neutral acetate of lead. The acid contains, at 100°, 75·03 p. c. C., 8·77 H., and 16·20 O.; the fused acid 77·08 p. c. C., 8·70 H., and 14·22 O.; the lime-salt 10·26 p. c. CaO.; the silver-salt 41·78 to 43·58 p. c. AgO. Johnston gives the formula $C^{40}H^{27}O^6$ (Johnston, *Phil. Mag.* 12, 560; *Phil. Trans.* 1840, 347; *J. pr. Chem.* 14, 437; 26, 146). See also Cerutti (*N. Br. Arch.* 22, 186).

21. RETINITE. *Walchovite.* — Occurs in the coal-mines of Walchow, in Moravia, in rounded pieces of the size of a bean to that of the head. Yellow, with conchoïdal fracture and fatty lustre. Brittle. Sp. gr. 1·035 to 1·069. Becomes translucent and elastic at 140°, without melting, and melts to a clear oil at 250°. When subjected to dry distillation it yields combustible gas, tar, and aqueous ammonia. Combustible. Alcohol takes up 1·5 p. c., ether 7·5 p. c. of resin: both resins are transparent, yellow, and tough. Retinite softens in bisulphide of carbon, but dissolves only to a slight extent: it is likewise very slightly soluble in boiling rock-oil. — Contains 80·40 p. c. C., 10·68 H., and 8·74 O., corresponding to the formula $C^{40}H^{31}O^{3·3}$ (Schrötter, *Pogg.* 59, 61). See also Cerutti (*N. Br. Arch.* 22, 286).

Retinite occurs in reddish-yellow brittle layers in the lignite of the Wilhelmszeche mine in the Westerwald: the branchite or scheererite found in the same place, likewise passes into a resin, which has the colour and soft waxy quality of retinite (see above), and does not melt at 225°, but becomes brittle on cooling, and dissolves completely in alcohol and ether (Casselmann).

22. SCHLERETINITE. A fossil resin from the coal-mines of Wigan. Black drops and granules, sometimes as big as nuts, brittle, and of conchoïdal fracture. Sp. gr. 1·136. Combustible. By dry distillation it yields water and a large quantity of empyreumatic oil, and leaves a residue of charcoal. It is insolüble in water, alcohol, ether, and alkalis, and is slowly decomposed by strong nitric acid. When it is reduced to fine powder and boiled with water, alcohol, and ether in succession, traces of oil are dissolved, after which it contains at 120°, on the average, 3·68 p. c. of ash, 76·95 p. c. C., 8·95 H., and 10·42 O., corresponding to the formula $C^{40}H^{28}O^4$ (Mallet, *Phil. Mag.* (4) 4, 261; *Ann. Pharm.* 85, 135). — This body was erroneously regarded by Dana and Mallet as identical with Rochleder's pyroretin. See Kenngott (*Kenng. Jahrbuch.* 1855, 117).

23. RESIN OF SETTLING STONES. From the refuse of a lead-mine in Northumberland. Partly black and partly amber-yellow, and red or

brown-red within. Hard, brittle, and of conchoïdal fracture. Sp. gr. 1·16 to 1·54. — Does not melt at 105°. Yields by dry distillation a little transparent rock-oil, and afterwards a red empyreumatic oil, leaving a large quantity of charcoal. Burns in the air, emitting dense fumes and an aromatic, slightly burnt odour. — Dissolves slowly but completely in strong nitric acid, and very slightly in alcohol and ether (Johnston, *Ed. N. Journ. of Sc.* 4, 122 : further *J. pr. Chem.* 17, 108).

|        |     |     |        |     | Johnston. |
|--------|-----|-----|--------|-----|-----------|
| 80 C   | 480 | ... | 85·41  | ... | 85·29     |
| 66 H   | 66  | ... | 11·74  | ... | 11·03     |
| 2 O    | 16  | ... | 2·85   | ... | 3·68      |
| $C^{80}H^{66}O^2$ | 562 | ... | 100·00 | ... | 100·00 |

The above is the composition after deducting 3·25 p. c. of ash. According to Johnston, the body is probably free from oxygen, and of the formula $C^4H^3$.

24. TASMANNITE. — From the banks of the Mersey, Tasmania. It is separated from earthy impurities by digesting it with strong hydrochloric acid, the density of which is increased by the addition of chloride of calcium, and by levigation. It is transparent and brown-red, has a resinous lustre and a conchoïdal fracture. After deducting ash it contains 79·34 p. c C., 10·41 H., 5·32 S., and 4·93 O., corresponding to the formula $C^{80}H^{62}S^2O^4$. — By dry distillation it yields an oil and a solid product. Burns easily with a smoky flame and a disagreeable odour. It is slowly attacked by nitric acid, but is not decomposed by hydrochloric acid. It is not altered by alkalis, and is insoluble in bisulphide of carbon, alcohol, ether, benzene, oil of turpentine, and coal-oil (Church, *Phil. Mag.* [4] 28, 465 ; *Zeitschr. Ch. Pharm.* 8, 137).

25. RESINS OF PEAT. A. *From compact Friesland peat.* When peat which has been exhausted with boiling water is boiled with alcohol, a brown solution is obtained, whilst *delta-resin* remains in the peat and may be extracted by rock-oil. The alcoholic solution deposits on cooling grey flocks of *gamma-resin*, which may be purified by redissolving them in boiling alcohol and cooling, and afterwards precipitating the hot alcoholic solution with alcoholic neutral acetate of lead, filtering from the precipitate, cooling the filtrate, and dissolving the flocks which separate in ether. The alcoholic mother-liquor holds in solution *alpha-* and *beta-resins*, the former of which (after evaporating the solution to dryness, boiling with water, and dissolving in a little alcohol) may be thrown down as a grey-black precipitate by alcoholic basic acetate of lead, and the latter precipitated from the filtrate by water in grey-green flocks free from lead.

The *alpha-resin* forms a lead-salt containing 56·55 p. c. C., 7·81 H., and 21·42 PbO., corresponding to the formula $C^{80}H^{40}O^9$,PbO. — The *beta-resin* is gall-green, sticky, melts at 52°, is easily soluble in alcohol and ether, soluble with red colour in oil of vitriol, insoluble in boiling caustic potash, and difficultly decomposible by strong nitric acid. It contains, at 100°, 76·31 p. c. C., 10·98 H., and 12·71 O., corresponding to the formula $C^{77}H^{67}O^9$. — The *gamma-resin* is white, brownish when dried, waxy, and melts at 74°. It dissolves in oil of vitriol, forming a solution precipitable by water, and is soluble in warm caustic potash from which it is precipitated by acetic acid: it does not dissolve in cold alcohol. It contains, at 100°, 78·05 p. c. C., 11·94 H., and 10·01 O.,

corresponding to the formula $C^{104}H^{94}O^9$. — The *delta-resin* is deep-brown, brittle, melts at 68°, and is insoluble in boiling alcohol and hot caustic potash, but soluble in ether and rock-oil. It contains, at 100°, 79·70 p. c. C., 12·15 H., and 8·15 O., corresponding to the formula $C^{131}H^{121}O^9$ (Mulder (*J. pr. Chem.* 16, 495 ; 17, 444).

B. The *light Friesland peat* yields in like manner an alpha-resin soluble in cold alcohol, and a gamma-resin insoluble therein. — The *alpha-resin* is black, sticky, fusible at 55°, soluble with red colour in oil of vitriol, and slightly soluble in caustic potash. It is precipitated by alcoholic basic acetate of lead, and is soluble in ether. It contains 75·12 p. c. C., 10·21 H., and 14·67 O., corresponding to the formula $C^{35}H^{28}O^5$. — The *gamma-resin* is brittle, fusible at 74°, insoluble in caustic potash, and very easily decomposed by nitric acid. It dissolves in rock-oil, ether, and in a large quantity of boiling alcohol, from which it is deposited on cooling. Contains, at 100°, 79·43 p. c. C., 12·54 H., and 8·03 O. Water throws down from its solution in oil of vitriol a precipitate containing sulphuric acid (Mulder, *J. pr. Chem.* 17, 449).

26. XYLORETIN. — In the fossil pine-trunks of Danish peat-bogs. When these are exhausted with alcohol, the solution evaporated, the residue again dissolved in ether, and the ether allowed to evaporate slowly, the xyloretin separates in indistinct crystals, which melt at 165° and are not volatile without decomposition. It evolves hydrogen with potassium, and forms a potash-salt crystallisable from alcohol. Contains, on the average, 78·97 p. c. C., 10·87 H., and 10·16 O., corresponding to the formula $C^{40}H^{32}O^4$ (Forchhammer, *Ann. Pharm.* 41, 42). See also *Boloretin* (p. 435), retene (p. 8), and *Tehoretin* (under *Fichtelite*).

Schrötter (*Pogg.* 59, 54), by exhausting wood from the peat-beds of Redwitz in the Fichtelgelbirge with ether, and evaporating the solution, obtained crystals melting at 145° to 160°, whilst an oil having the composition $C^{40}H^{20}$ or $C^{40}H^{32}$ (88·58 p. c. C., 11·34 H.) remained in solution. The crystals contain 79·75 p. c. C., 10·03 H., and 9·22 O., and according to Schrötter, are xyloretin. Retene (p. 8) and fichtelite, $C^{80}H^{70}$, have also been found near Redwitz.

## 27. Resins from the Lignite of Weissenfels.

WACKENRODER. *N. Br. Arch.* 60, 23 ; abstr. *Ann. Pharm.* 72, 315. BRÜCKNER. *J. pr. Chem.* 57, 1.

The lignite-beds of Gerstewitz near Weissenfels (Saxony) contain layers of opaque, dull, greyish-brown or yellow friable masses, of sp. gr. 0·493 to 0·522, Kenngott's *Pyropissite*, from which alcohol extracts wax-like substances, and which yield by dry distillation as much as 62 p. c. of paraffin (see below) (Kenngott & Marchand, *Lieb. Kopp's Jahresber.* 1850, 764). This pyropissite was, doubtless, the material employed in Wackenroder's and Brückner's investigations.

Wackenroder's *Cerinin* is extracted from pyropissite by ether, and remains on evaporating the solution, as a soft pasty wax, which becomes fluid at 100°, and contains 78·2 p. c. C., 12·3 H., and 9·5 O., corresponding to the formula $C^{40}H^{38}O^4$, but is probably a mixture.

**1.** *Leucopetrin.* — An ethereal extract of the yellow-brown lignite leaves on evaporation a wax from which boiling 80 p. c. alcohol takes up 80 p. c., chiefly georetic acid, whilst leucopetrin remains undissolved. It is purified by crystallisation from boiling absolute alcohol. — Colourless tufts of needles which melt at 100°, turning brown and decomposing. When treated with warm fuming nitric acid, it evolves a large quantity of red fumes, without dissolving. It turns brown when warmed with oil of vitriol and carbonises on boiling. It is insoluble in caustic potash, soluble in 268 parts of cold absolute alcohol, and more easily in ether; soluble also in rock-oil and oil of turpentine. Insoluble in 80 p, c. alcohol.

| | Calc. according to Brückner. | | | | Brückner. at 100°. | |
|---|---|---|---|---|---|---|
| 50 C | 300 | ........ | 81·97 | ........ | 81·69 | ........ | 82·00 |
| 42 H | 42 | ........ | 11·47 | ........ | 11·41 | ........ | 11·48 |
| 3 O | 24 | ........ | 6·56 | ........ | 6·90 | ........ | 6·52 |
| $C^{50}H^{42}O^3$ | 366 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Or perhaps $C^{68}H^{56}O^4$? (by calc. 82·26 C., 11·28 H., 6·46 O.) (Kr.).

**2.** *Georetic acid.* — The alcoholic solution obtained in 1 solidifies to a jelly on cooling, from separation of wax, which is completely removed by concentrating and cooling the solution. From the brown alcoholic mother-liquor, alcoholic neutral acetate of lead throws down a brown precipitate of georetic acid, whilst a resin still remains in solution. The precipitate is washed with alcohol and decomposed by strong acetic acid, and the georetic acid is allowed to crystallise from alcohol. — It forms small white needles, which dissolve in alcoholic ammonia and are left free from ammonia on evaporation. Dissolves easily in boiling alcohol. The alcoholic acid forms with acetate of copper a dirty-green precipitate containing, at 100°, 12·63 p. c. CuO (calc. for $C^{24}H^{21}CuO^8$ requires 12·14 CuO.).

| | Lead-salt at 100°. | | | | Brückner. |
|---|---|---|---|---|---|
| 24 C | 144 | ........ | 43·28 | ........ | 43·36 |
| 21 H | 21 | ........ | 6·31 | ........ | 6·59 |
| 7 O | 56 | ........ | 16·84 | ........ | 15·47 |
| PbO | 111·7 | ........ | 33·57 | ........ | 34·58 |
| $C^{24}H^{21}PbO^8$ | 332·7 | ........ | 100·00 | ........ | 100·00 |

**2a.** The solution filtered from the lead-salt of georetic acid, when freed from lead by hydrosulphuric acid, still contains a soft, pulverulent resin, which is deposited, on evaporating the solution, in white light granular masses containing 77·35 p. c. C. and 10·20 H., and approximately represented by the formula $C^{60}H^{40}O^6$.

**3.** *Geomyricin.* — When the dark-brown lignite is exhausted with cold alcohol of 80 p. c. to remove georetic acid and other substances, and afterwards boiled with alcohol of the same strength, the filtrate, before it is quite cold, throws down geomyricin in the form of a powder, quickly followed by a gelatinous deposit of geocerain. The former body is obtained more abundantly by boiling the lignite-residue with absolute alcohol, and may be purified by recrystallisation. Light, white powder, made up of microscopic capillary crystals. Melts to a

yellow, very brittle wax at 80—83°. Burns with a luminous flame. It is not acted upon by solution of caustic potash, but is attacked by the fused hydrate.

|  |  |  |  |  | Brückner. mean. |
|---|---|---|---|---|---|
| 68 C | 408 | ............ | 80·31 | ............ | 80·27 |
| 68 H | 68 | ............ | 13·38 | ............ | 13·37 |
| 4 O | 32 | ............ | 6·31 | ............ | 6·36 |
| $C^{68}H^{68}O^4$ | 508 | ............ | 100·00 | ............ | 100·00 |

4. *Geoceric acid.* — The solution in boiling alcohol of 80 p. c. obtained in 3, after being freed from geomyricin, still contains geoceric acid and georceraïn, the former of which may be precipitated from the boiling solution by alcoholic neutral acetate of lead, whilst the geoceraïn is deposited from the filtrate on cooling. The lead-salt is boiled with alcohol of 80 p. c., absolute alcohol, and ether, in succession, and then decomposed by acetic acid, and the geoceric acid thereby separated is purified by crystallisation. — White lamellar shining mass, melting at 82°, and very brittle and friable after fusion. — Dissolves freely in hot alcohol and is deposited almost completely from the solution on cooling in the form of a non-crystalline jelly.

|  |  |  |  |  | Brückner. mean. |
|---|---|---|---|---|---|
| 56 C | 336 | ............ | 79·24 | ............ | 78·64 |
| 56 H | 56 | ............ | 13·21 | ............ | 12·70 |
| 4 O | 32 | ............ | 7·55 | ............ | 8·66 |
| $C^{56}H^{56}O^4$ | 424 | ............ | 100·00 | ............ | 100·00 |

|  | Lead-salt. |  |  |  | Brückner. |
|---|---|---|---|---|---|
| 56 C | 336 | ............ | 63·79 | ............ | 63·82 |
| 55 H | 55 | ............ | 10·63 | ............ | 10·41 |
| 3 O | 24 | ............ | 4·38 | ............ | 4·69 |
| PbO | 112 | ............ | 21·20 | ............ | 21·08 |
| $C^{56}H^{55}PbO^4$ | 527 | ............ | 100·00 | ............ | 100·00 |

5. *Geoceraïn.* — This body is freed from geomyricin by dissolving it in boiling 60 p. c. alcohol, in which geomyricin is insoluble, and from adhering lead by means of hydrosulphuric acid. — It forms white lamellar masses fusible to a yellow wax at 80°. Contains 79·11 p. c. C., and 13·07 H., and is therefore isomeric with geoceric acid.

6. *Geocerinone.* — Both the yellow and the dark-brown lignite, when submitted to dry distillation, yield gases and a buttery distillate, from a solution of which in boiling alcohol of 80 p. c., geocerinone crystallises on cooling. — It forms pearly six-sided tables, melting at 50° and burning with luminous flame. — Dissolves in warm oil of vitriol, and turns brown and carbonises when heated. It is slightly attacked by fuming nitric acid. A hot saturated solution of bichromate of potash, with addition of oil of vitriol, produces a copious evolution of carbonic acid, with a smell of butyric acid, whilst sesquioxide of chromium and an acid precipitable from its alcoholic solution by neutral acetate of lead are formed. — Dissolves slightly in boiling 80 p. c. alcohol, and easily in absolute alcohol and ether.

|        |     |  |        |  | Brückner. |
|--------|-----|--|--------|--|-----------|
|        |     |  |        |  | *mean.*   |
| 110 C ............ | 660 | ............ | 83·97 | ............ | 83·97 |
| 110 H ............ | 110 | ............ | 14·00 | ............ | 14·07 |
| 2 O ............ | 16 | ............ | 2·03 | ............ | 1·96 |

| $C^{110}H^{110}O^2$ .... | 786 | ............ | 100·00 | ............ | 100·00 |

According to Brückner, it is the ketone of geoceric acid.


## D.   *Resins extracted from plants.*


*Soft resin of Althæa.* — (Trommsdorff, *N. Tr.* 19, 1, 176).

*Resin of Anacahuita-wood.* — The wood and bark (previously ex-hausted with water) are exhausted with very weak caustic potash; the solution is allowed to stand till clear, and the resin is precipitated by hydrochloric acid. The precipitate is digested with alcohol, the extract evaporated, and the residue boiled with water and dried. Con-tains, on the average, 60·25 p. c. C., 6·99 H., and 32·76 O., correspond-ing to the formula $C^{48}H^{34}O^{20}$ (L. Müller, *Pharm. Viertelj.* 10, 532).

*Acrid soft resin of the nut-shells of Anacardium occidentale.* — (De Mattos, *J. Pharm.* 17, 625).

*Resin of Angelica-root.* — An alcoholic tincture of angelica-root separates on evaporation into two layers, the lower of which is pale-yellow and watery, and contains a large quantity of sugar, the upper brown and resinous. The latter, after washing with water, forms Buchholz and Brandes' *Angelica balsam* (*N. Tr.* 1, 2, 138); it dissolves in alcohol and ether (Buchner), is quickly turned brown to black by cold oil of vitriol, but is not coloured by oil of vitriol in alcoholic solu-tion, and is thereby distinguished from sumbul balsam. When sub-mitted to dry distillation, it yields colourless and yellow oils, but no blue vapours, as is the case with sumbul balsam (Reinsch, *Repert.* 89, 299).

Angelica balsam boiled with caustic potash yields a distillate of volatile oil, the residue containing angelica wax, angelicin, and the potash-salt of angelic acid (x, 415) (Büchner).

*Angelicin.* — From Angelica balsam. The resin-soap formed by boiling angelica balsam with caustic potash, when evaporated and dis-solved in water, deposits wax, after the removal of which, on one occasion, angelicin crystallised from the solution. A more certain method of preparing it is to dissolve the resin-soap in alcohol, pass carbonic acid into the solution, evaporate, and treat the residue with ether, which takes up the angelicin. — Crystallises from alcohol in delicate colourless needles, inodorous, and at first tasteless, but after-wards burning and aromatic. Melts easily and creeps up the sides of a glass vessel without subliming. — Burns with smoky flame. When boiled with caustic potash, it melts and partially dissolves, the undis-solved portion crystallising on cooling; from the alkaline solution carbonic acid (and a stronger acid more quickly) precipitates white flocks. — Dissolves in alcohol and ether (Buchner, *Repert.* 76, 167).

*Angustura-bark* contains a *hard resin*, soluble in potash, alcohol, and

acetate of ethyl, insoluble in ether, rock-oil, and oil of turpentine ; and a greenish-yellow, *soft* resin, which assumes a cochineal-red colour with oil of vitriol, and is soluble in alcohol, ether, and fatty and volatile oils, but insoluble in caustic potash (Pfaff).

*Soft resin of Anthemis Pyrethrum* (John. — Gaultier, *J. Pharm.* 4, 49).

*Soft resin of Arnica montana* (John, *Chem. Schriften*).

*Soft resin of the buds of Aster glutinosus* (John, *Chem. Schriften*, 2, 79).

*Resin of the bark of Atherosperma moschatum.* — Obtained from the bark (previously exhausted with dilute sulphuric acid) in the same manner as the resin of anacahuita-wood. Brown-red ; melts at 114°. Dissolves easily in caustic alkalis and their carbonates, from which it is precipitated by acids, and also in alcohol, but is nearly insoluble in ether. Contains at 100°, on the average, 69·38 p. c. C., 8·85 H., and 21·77 O., corresponding to the formula $C^{42}H^{32}O^{10}$ (Zeyer, *Pharm. Viertelj.* 10, 517).

*Resin of Cannabis indica.* — When precipitated from the alcoholic solution by water, it is yellow-brown and narcotic, and acts like morphine, likewise producing contraction of the pupils (T. & H. Smith, *N. J. Pharm.* 11, 278). The narcotic resin occurs in greater quantity in *Cannabis indica* from Algeria than in that grown in France. It dissolves in alcohol, ether, and volatile and fixed oils (Decourtive, *N. J Pharm.* 13, 427). — When commercial *Extractum cannabis* is dissolved in cold alcohol of 83 p. c., filtered, mixed with water till cloudiness is produced, and digested with animal charcoal, then again filtered, and precipitated by water, and the precipitate thereby formed is dissolved in ether and the solution evaporated, a shining pale-brown resin is obtained, which becomes glutinous when exposed to sunshine, but after repeated melting, kneading, and cooling, becomes brittle and friable, and melts at 90°. It has a bitter taste and a narcotic odour. Insoluble in aqueous ammonia and caustic potash, but easily soluble in volatile oils. After boiling with acids, it reduces an alkaline solution of cupric oxide (G. Martius, *N. Repert.* 4, 534).

*Hard resin of Cascarilla* (Trommsdorff, *N. Tr.* 26, 2, 138).

*Resin of Centaurea benedicta* (Morin, *J. Chim. méd.* 3, 105).

*Resin of the bark of Cornus mascula* (Trommsdorff, *N. Tr.* 17, 1, 37).

*Soft resin of Cortex Corova* (Trommsdorff, *N. Tr.* 21, 2, 123).

*Resins of Cubebs.* — A. *Resin insoluble in potash,* probably formed by the oxidation of oil of cubebs (xvi, 272) ; it is also produced by digesting oil of cubebs with nitric acid and alcohol. — Coarsely powdered cubebs is freed from volatile oil as much as possible by distilling it with water, and afterwards exposing it to a current of superheated steam, and the insoluble residue is collected, dried, and exhausted with 94 p. c. alcohol, which takes up resins, cubebin, cubebic acid, and a little volatile oil, and leaves them behind on evaporation. This residue is heated to boiling with strong caustic potash, and diluted with a large

quantity of water, and after standing 24 hours, the alkaline liquid, which contains cubebic acid, is decanted from the resin which has separated, and the latter body is washed with hydrochloric acid and water, and dissolved in hot alcohol, whereupon cubebin (xvi, 273) crystallises on cooling. From the oily mother-liquor, which consists of a mixture of oil and resin, the oil is separated by boiling with water, and more completely by heating to 240°, and the remaining resin is then dissolved in alcohol, boiled with caustic potash, and with water, again dissolved in alcohol, decolorised by animal charcoal, and evaporated.

Pale, brownish-yellow, tasteless, soft resin, melting at 60°. It is violently attacked by fuming nitric acid, and reddened by oil of vitriol, and therefore probably still contains cubebin. Insoluble in aqueous alkalis; easily soluble in alcohol, ether, bisulphide of carbon, and chloroform (Bernatzik). See also Trommsdorff (*J. Pharm.* 21, 69); Dublanc (*J. Chim. méd.* 3, 491).

B. *Resin soluble in potash.* Bernatzik's *Cubebic acid.* Previously noticed by Monheim (xvi, 292), and distinguished as a waxy resin. — The alkaline solution obtained in the preparation of A is mixed with dilute sulphuric acid, till turbidity is produced, whereupon the still strongly alkaline solution deposits the cubebic acid on standing and subsequent concentration. The acid is redissolved in caustic potash, freed from the soft resin, which separates on diluting the solution, and precipitated by chloride of barium. The precipitate thus obtained is dissolved by repeated boiling with water; the solution is concentrated and decomposed by hydrochloric acid; and the precipitate is washed with boiling water. — *Extractum Cubebarum æther.:* on standing, throws down a crystalline deposit containing cubebic acid. It is thrown upon a filter to separate the remaining fluid portion, and then treated with ether or cold alcohol, which leaves cubebin. The tincture is submitted to distillation, the residue dissolved in caustic potash, and the solution precipitated with chloride of barium. The precipitate dissolved in boiling water or boiling alcohol yields crystals of the baryta-salt, from which the acid may be separated.

*Properties.* White, amorphous mass, resembling wax, sticky between the teeth. It softens in the hand, and melts at a somewhat higher temperature. Tastes like wax.

*Decompositions.* Turns brown in the *air.* — Dissolves in *oil of vitriol,* forming a fine purple-violet solution, which turns brown at 90° to 100°, and afterwards blackens; water precipitates from the violet solution violet-grey flocks, which dissolve in alkalis with green, and in alcohol with red colour. No sugar is formed thereby, or by boiling with hydrochloric acid. — Sulphuric acid, added to a solution of the potash-salt of the acid mixed with bichromate of potash, throws down at first a resin, which on the addition of more acid and warming, dissolves to a deep green liquid, and is not precipitated by water. — The acid is dissolved by *nitric acid* of 40 p. c., only on warming, and by the fuming acid in the cold, with yellow colour; excess of alkali colours this solution (or a solution of the potash-salt mixed with excess of fuming nitric acid) blood-red, without precipitating the cubebic acid.

The acid is insoluble in cold, and very slightly soluble in boiling *water.* — It dissolves very slightly in weak or strong *caustic potash* and *soda* in the cold, but on boiling it with a strong solution and afterwards diluting, a clear solution is obtained, from which a salt of the acid is

deposited on concentration. The salts of the alkalis separate from moderately strong aqueous solutions, or from solution in alcohol, in crystals which dissolve to a turbid alkaline liquid in water. Mineral acids throw down cubebic acid from its alkaline salts in the form of a white resin, long before the solution ceases to be alkaline. — The acid dissolves in *ammonia-water* only on warming, and is precipitable by water or aqueous alkalis.

*Baryta-salt.* — Preparation see above. Obtained from boiling water or alcohol in white crystalline groups, which form a turbid solution in water.

*Magnesia-salt.* — The alkaline salts of cubebic acid throw down from magnesia-salts an amorphous white precipitate, which melts when warmed. It turns brown in the air, and is insoluble in boiling water.

The alkali-salts of cubebic acid precipitate *metallic salts.*

The acid dissolves easily in *chloroform, alcohol,* and *ether* (Bernatzik, *N. Repert.* 14, 98).

*Resin of Fern-root.* — Geiger (*Mag. Pharm.* 17, 78).

*Acrid resin of Jatropha Curcas.* Soubeiran (*J. Pharm.* 15, 504; *Br. Arch.* 33, 207).

*Acrid soft resin of the root of Iris florentina.* A. Vogel (*J. Pharm.* 1, 184).


# Resins of Juniper-berries.

*Resins of Juniper-berries.* — Contained in the old, but not in the fresh berries, being formed from volatile oil (Rebling, *N. Br. Arch.* 67, 228). — *a.* The resin obtained by boiling the alcoholic extract with water is dingy-green, brittle, and triturable to a grey-green powder. Has a faint odour of juniper-berries, but no taste; softens and melts when warmed. In boiling potash-ley it becomes harder and more compact, without dissolving. It dissolves in cold aqueous ammonia, forming a light green solution, from which it is precipitated by acids. It dissolves in alcohol, ether, and volatile oils, less easily in fixed oils (Trommsdorff).

*b.* Steer's *Juniperin.* When juniper-berries, after being washed out with water, are distilled to obtain the volatile oil, the residue, if strained while hot, deposits in the still, on cooling and evaporation, a sediment, which must be treated with cold and boiling alcohol in succession. The resulting extracts, when cooled and distilled, deposit successively wax and green resin, and finally juniperin as a yellow powder, which then cakes together to a resin, and as such is separated and washed. It is converted, by trituration with water, into a yellow powder, which dissolves completely in 60 pts. of water, and is taken up by ether when agitated therewith. The juniperin left on evaporation of the ether is light yellow, and burns with flame, emitting the odour of juniper. It dissolves in oil of vitriol with light yellow colour, changing to red-brown on standing, and in ammonia with gold-yellow colour (Fr. Steer, *Wien. Acad. Ber.* 21, 383).

*Resin of Laurel.*   Bonastre (*J. Pharm.* 10, 30).

*Resins of the bark of Lopez-root.*   The ethereal extract, washed with water, is resolved by cold alcohol into a sparingly soluble resin, melting at 170°, and containing 64·25 p. c. C., and 7·99 H., and an easily soluble resin melting at 48°, containing 69·54 p. c. C., and 7·43 H.   Both resins are soluble in caustic potash, and precipitable therefrom by acids, and are not decomposible by acids with formation of sugar. — An alcoholic extract of the bark which has been exhausted with ether leaves on evaporation a third resin, which, after washing with warm water, is brittle and tasteless, melts at 135°, and contains 62·38 p. c. C., and 3·92 H.   It dissolves freely in aqueous alkalis, from which it is precipitated by acids; does not form sugar, and is nearly insoluble in ether (Schnitzer, *Pharm. Viertelj.* 11, 1).

*Resin of Lycoperdon cervinum.*   Biltz (*N. Tr.* 11, 2, 58).

*Acrid resin of Manna.* — Manna is suspended in an equal weight of water, and shaken repeatedly with ether, which takes up the resin, together with a little acid (both in very small quantity).   The yellow ethereal solution leaves on evaporation a yellow resin, which is washed with water, and dissolved in hot absolute alcohol.   The alcoholic solution, separated from the white powder deposited on cooling, is rendered milky by water: it is coloured darker, and precipitated by ammoniacal nitrate of silver, only on standing for some time, and yields with alcoholic neutral acetate of lead, especially on addition of ammonia, a brown precipitate, which on one occasion contained 35·75 p. c. C., 4·46 H., 13·15 O., and 46·64 PbO, and on another occasion, 25·27 p. c. C., 3·12 H., 13·19 O., and 58·42 PbO (Leuchtveiss, *Ann. Pharm.* 53, 131).

*Resin of Medicago.*   Bernays (*Repert.* [3] 6, 329).

*Acrid resin of Radix Meu.*   Reinsch (*Jahrb. pr. Pharm.* 2, 302; 14, 388).

*Resin of the Brazilian Clove (Persea caryophyllata).*   Trommsdorff (*N. Tr.* 23, 1, 12).

*Resin of Oenanthe crocata.*   Cormerais (*J. Chim. méd.* 6, 459).

*Resin of Oenanthe fistulosa.*   Gerding (*J. pr. Chem.* 44, 175).

*Resins of Grana Paradisi.* — Grains of Paradise contain a resin precipitable from the alcoholic solution by alcoholic neutral acetate of lead, and a second resin not precipitable (Sandrock, *N. Br. Arch.* 73, 18).

*Resin of Spanish pepper.*   *Capsicin.* — Obtained as a yellowish-red or red-brown, thick resin, having an extremely burning taste, by exhausting the alcoholic extract of the pepper with ether, and evaporating the solution.   It becomes thicker in sunlight.   Dissolves slightly in water, to which it communicates its harshness.   It dissolves easily, with red-brown colour, in caustic potash, alcohol, ether, and oil of turpentine: hardens to a solid compound with baryta (Buchholz, *Taschenbuch*, 1816, 1; Braconnot, *Ann. Chim. Phys.* 6, 1, and 122; *Repert.* 26, 157).   Dilute acids extract from the red-brown resin a

poisonous non-alkaline substance, which inflames the skin : it does not yield crystals with acids, and is precipitated from its solutions by alkalis in yellowish-brown flocks (Landerer, *Pharm. Viertelj.* 3, 34).

*Resins of Petasites vulgaris.* — The alcoholic tincture of the dried root, when submitted to distillation, leaves a sticky mass, consisting of petasite balsam. When this is boiled for some hours with moderately strong caustic soda, a portion of it (the petasitic acid) dissolves, whilst a volatile oil is driven off, and a pale-yellow resin, Reinsch's petasite, remains undissolved. The two bodies are separated ; the alkaline solution is precipitated by phosphoric acid ; and the yellow-brown flocks are collected, washed with water, dissolved in alcohol, and the solution is left to evaporate. *Petasitic acid* forms brown crystalline flocks, having an acrid, harsh taste : it gradually turns brown with hydrochloric or sulphuric acid, dissolves in dilute caustic soda, and yields a volatile oil by dry distillation. — *Petasite* smells like the root, is not acted on by strong caustic soda, and yields by dry distillation, a yellow oil having an odour of radishes. Its alcoholic solution mixed with a little hydrochloric or sulphuric acid, assumes a fine emerald-green colour, which changes to blue, and ultimately to brownish-green, when hydrochloric acid is employed (Reinsch, *N. Jahrb. Pharm.* 4, 257).

*Resins of Pimpinella Saxifraga.* Bley (*N. Tr.* 12, 2, 80).

The resin of the root of *Podophyllum peltatum (Podophyllin)* is obtained by evaporating the alcoholic tincture to a syrup, precipitating with water, and washing. It is very bitter, and acts as a purgative. It dissolves in alcohol and ether, and is partially saponified by alkalis. — Ether extracts from the root a black, less active resin (Cadbury, *Pharm. Journ.* 18, 179 ; *Chem. Centr.* 1859, 46).

*Resins of Poplar-buds.* — From the buds of the black poplar : Pellerin (*J. Pharm.* 8, 434) ; Schrader (*A. Gehl.* 6, 578) ; from the buds of *Populus balsamifera :* Hegström (*Crell. N. Entd.* 3, 171) ; from the bark : Wittstein, *Pharm. Viertelj.* 6, 47). Hallwachs obtained from poplar-buds, the crystals already mentioned (xv, 444) ; Piccard obtained chrysic acid, $C^{22}H^8O^6$ (*Züricher Milth., J. pr. Chem.* 93, 369 ; *Zeitschr. Ch. Pharm,* 8, 138).

*Acrid soft resin from Semen Ricini.* Soubeiran (*J. Pharm.* 15, 507).

## Resins of Squill (Scilla Maritima).

The investigations on *Scillitin,* the active ingredient of the bulb of *Scilla maritima (Handbuch.* viii., [2], 87), have not determined whether it is to be classed with the resins, the alkaloïds, or the bitter principles. — Mandel (*Compt. rend.* 51, 87) distinguishes two peculiar bodies, the poisonous and irritating *sculeïn,* and the non-poisonous scillitin, but adds nothing further concerning them. Schroff (*N. Repert.* 14, 241) also distinguishes a narcotic principle (*scillitin*) and an acrid non-volatile principle. Righini (*Repert.* 63, 87) regards scillitin as impure veratrin.

*a.* According to Tilloy (*J. Pharm.* 12, 635. — *N. J. Pharm.* 23, 406 ; *Pharm. Centr.* 1854, 93) squill contains no volatile acrid principle,

but crystals of citrate [oxalate (Schroff)] of lime, which irritate and inflame the skin when rubbed upon it. The active constituents are an acrid resin and a bitter substance.

Dried squill-powder gives up to ether an agreeably-smelling yellow fat (or fatty acid?) which may be freed from adhering bitter substance by means of hot water. When the powder which has been exhausted with ether is exhausted with alcohol, a very acrid and bitter tincture is obtained, leaving on evaporation an acrid resin, which is freed from adhering fat by ether, and from sugar by water. This resin is very poisonous; it softens in hot water, dissolves in alkalis and alcohol, and is not altered by acids. — The bitter substance is extracted by hot water from squill previously treated with ether and alcohol; it is precipitated from the liquid by charcoal, which gives it up again to boiling alcohol (Tilloy).

*b.* Vogel (*Schw.* 6, 101) and Lebourdais (*N. Ann. Chim. Phys.* 24, 62; *Ann. Pharm.* 67, 252) prepare the bitter substance as follows :—

1. Vogel exhausts the concentrated juice with alcohol, evaporates the tincture, dissolves the residue in water, precipitates tannic acid with neutral acetate of lead, removes excess of lead by means of hydrosulphuric acid, again filters, and evaporates. There then remains scillitin, together with sugar and salts, in the form of a colourless, friable mass, which has a very bitter, afterwards sweetish taste, and causes vomiting and purging. This mass softens quickly in the air, and dissolves easily in water and absolute alcohol, and in vinegar. — 2. Lebourdais precipitates the highly coloured and very viscid decoction of squill with neutral acetate of lead, and agitates the cold filtrate with purified animal charcoal till it loses its colour and bitterness. The charcoal is then washed and dried, and boiled with alcohol, which takes up the scillitin, and leaves it behind on evaporation. — Amorphous, neutral, non-hygroscopic mass, which decomposes easily when heated, dissolves with purple colour in oil of vitriol, afterwards blackening, and is decomposed by nitric acid. — A portion placed upon the tongue produces the sensation of a caustic. — Bley (*N. Br. Arch.* 61, 141) operated in the same way as Lebourdais, avoiding too great heat, and obtained by spontaneous evaporation, long colourless flexible needles, having a very bitter taste, becoming amorphous when gently warmed, and not afterwards susceptible of crystallisation. — According to Wittstein (*Repert.* [3] 4, 200), the bitter of squill is not precipitable by basic acetate of lead, nor by hydrated oxide of lead, which latter, however, precipitates the acrid constituent.

*c.* Marais (*N. J. Pharm.* 31, 130) and Landerer (*Repert.* 47, 442) believed they had obtained an alkaloïd, which Tilloy was not able to isolate.

1. Marais exhausts either the dried squill with 56 p. c. alcohol, or the fresh bulbs with alcohol of 90 p. c., mixes the tincture with milk of lime, agitates with ether, separates the supernatant layer of liquid, and evaporates, whereupon scillitin and fat remain, the latter of which is removed by again dissolving the residue in alcohol. — Amorphous, hygroscopic, pale-yellow mass, having a penetrating bitter taste, and an alkaline reaction. — It dissolves in oil of vitriol, forming a violet solution, from which water precipitates green flocks, and in nitric acid with red colour, which quickly disappears; it is insoluble in hydro-

chloric acid, but soluble in ammonia and caustic alkalis, becoming decomposed and losing its bitter taste. When heated with hydrate of potash, it evolves ammonia. It does not dissolve in water. Produces with sesquichloride of iron an orange-yellow, and with bichloride of platinum a yellow precipitate, and combines with acetic acid. It dissolves in alcohol and ether. Taken internally, it acts as an emetic and violent purgative, and afterwards as a narcotic (Marais). — 2. Landerer digests the crushed inner portions of squill with very dilute sulphuric acid, boils down the filtrate to one-half, saturates it with lime. and sets it aside for three days ; then collects and dries the residue, When this residue is boiled with alcohol, the filtrate deposits on evaporation a very small quantity of extremely bitter needles, which are insoluble in water, and sparingly soluble in alcohol. The needles have an alkaline reaction and neutralise acids, forming therewith crystalisable salts, which melt when heated (evolving vapours which excite coughing), and carbonise, but do not leave a trace of lime. This body does not appear to be obtained from dried squill.

*Resin of Radix Sumbulus. Sumbul balsam.* — When an ethereal extract of the root is evaporated, and the residue is freed from wax by dissolving it in 75 p. c. alcohol and again evaporating, there remains a clear pale-yellow mass of the consistence of Venice turpentine ; Reinsch's *sumbul balsam.* A few drops of this body, heated in a warm glass tube assume an olive-green, afterwards indigo-blue colour. When submitted to dry distillation, it yields a yellow and a green oil, and at last a dark-blue oil which, according to Sommer (*N. Br. Arch.* 98, 1), contains umbelliferone, the retort at the same time being filled with blue vapours. — On dropping the balsam into oil of vitriol, the liquid assumes a fine purple colour, whereupon water throws down blue flocks. Oil of vitriol likewise produces a lilac or purple precipitate in the alcoholic solution. — When the balsam is melted with pieces of caustic potash, and the mass is treated with a little water, angelate of potash (x, 415) is dissolved, whilst sumbulamate of potash remains behind. The latter body, when dissolved in water and decomposed by dilute sulphuric acid, yields sumbulamic acid in the form of a turpentine-like mass, which crystallises in soft yellow needles on standing for some weeks. Its potash-salt is crystalline ; its solution in absolute alcohol acquires a violet to blue colour when hydrochloric acid gas is passed into it, and yields by distillation a colourless oil which may be freed from acid by carbonate of potash, and is coloured violet or blue by oil of vitriol : probably the vinic ether of sumbulamic acid (Reinsch, *Jahrb. pr. Pharm.* 6, 300 ; 7, 79 ; 13, 68).

*Resin of Taraxacum officinale.* Polex (*N. Br. Arch.* 19, 51).

*Resin of the Tea plant.* Mulder (*Pogg.* 43, 633).

*Resin of Tormentil root.* Meissner (*Berl. Jahrb.* 29, 2, 69).

*Hard resin of blue Grape-skins.* Nees v. Esenbeck (*Br. Arch.* 20, 196).

*Acrid Resin of Truffles.* Riegel (*Jahrb. pr. Pharm.* 7, 226).

*Turpeth-resin.* (Appendix to xvi, 405.) From the root of *Ipomœa Turpethum.* The root yields 4 p. c. of resin, $\frac{1}{20}$th of which is soluble in ether.

The root is exhausted with cold water and dried, afterwards coarsely comminuted and exhausted with alcohol. After distilling off the alcohol from the brown tincture, the resin is precipitated by water, and repeatedly boiled with water and dried, then shaken four or five times with ether, and precipitated from the alcoholic solution with ether an equal number of times. The resin thus obtained is *turpethin*.

Brown-yellow, inodorous, tasteless at first, afterwards bitter. Cannot be decolorised. Triturable to a greyish powder, extremely irritating to the mucous membranes. Melts at 183°.

|       |       |     |        |     |  | Spirgatis. mean (4). |
|-------|-------|-----|--------|-----|--|-----------|
| 68 C | 408 | ............ | 56·66 | ............ | | 56·60 |
| 56 H | 56  | ............ | 7·77  | ............ | | 7·81 |
| 32 O | 256 | ............ | 35·57 | ............ | | 35·59 |
| $C^{68}H^{56}O^{32}$ .... | 720 | ............ | 100·00 | ............ | | 100·00 |

Of the same composition, therefore, as jalapin (xvi, 407) and scammonin (xvi. 405) but distinguished therefrom by its insolubility in ether.

Turpethin *melted* on platinum-foil acquires a brown or black colour, evolves an acrid odour, takes fire, and burns with a bright smoky flame, leaving charcoal. It dissolves slowly in *oil of vitriol*, forming a fine red solution, which is coloured by water first a deeper red and afterwards brown and black. — It is decomposed by boiling with *mineral acids* into turpetholic acid and sugar:

$$C^{68}H^{56}O^{32} + 12\,HO = C^{32}H^{32}O^8 + 3\,C^{12}H^{12}O^{12}.$$
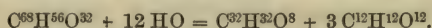
Under the influence of strong *bases* it takes up water and forms salts of turpethic acid.

Turpethin dissolves easily in *alcohol*, but not in *ether* (Spirgatis, *N. Repert.* 13, 97 ; *J. pr. Chem.* 92, 97.

*Turpethic acid.* — Obtained from turpethin by dissolving it in baryta-water, in the same manner as jalapic acid is obtained from jalapin. — Amorphous, yellow, shining, translucent, very hygroscopic mass. — Inodorous, and of sourish bitter taste. Has a strongly acid reaction.

|       |       |     |        |     |  | Spirgatis. mean. |
|-------|-------|-----|--------|-----|--|-----------|
| 68 O | 408 | ............ | 53·97 | ............ | | 53·88 |
| 60 H | 60  | ............ | 7·94  | ............ | | 7·90 |
| 36 O | 288 | ............ | 38·09 | ............ | | 38·22 |
| $C^{68}H^{60}O^{36}$ .... | 756 | ............ | 100·00 | ............ | | 100·00 |

Contains 1 at. HO more than jalapic acid.

Turpethic acid *burns* on platinum foil with a bright smoky flame. — When treated with mineral acids, it breaks up into turpetholic acid and sugar:

$$C^{68}H^{60}O^{36} + 8\,HO = C^{32}H^{32}O^8 + 3\,C^{12}H^{12}O^{12}.$$
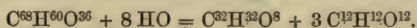
The sugar is susceptible of fermentation, tastes sweet, and smells of caramel when heated. — Turpethic acid dissolves in *water* (Spirgatis).

Turpethic acid forms a *semi-acid* and a *mono-acid* baryta-salt.

| | | | | | | Spirgatis. |
|---|---|---|---|---|---|---|
| | | *Semi-acid.* | | | | |
| 68 C | ........ | 408 | ........ | 45·78 | ........ | 45·58 |
| 58 H | ........ | 58 | ........ | 6·51 | ........ | 6·63 |
| 34 O | ........ | 272 | ........ | 30·52 | ........ | 30·49 |
| 2 BaO | ........ | 153 | ........ | 17·19 | ........ | 17·30 |
| $C^{68}H^{58}Ba^2O^{36}$ | .... | 891 | ........ | 100·00 | ........ | 100·00 |

| | | | | | | Spirgatis. |
|---|---|---|---|---|---|---|
| | | *Mono-acid.* | | | | |
| 68 C | ........ | 408 | ........ | 49·54 | ........ | 49·55 |
| 59 H | ........ | 59 | ........ | 7·16 | ........ | 7·22 |
| 35 O | ........ | 280 | ........ | 34·00 | ........ | 34·10 |
| BaO | ........ | 76·5 | ........ | 9·30 | ........ | 9·13 |
| $C^{68}H^{59}BaO^{36}$ | .... | 823·5 | ........ | 100·00 | ........ | 100·00 |

*Turpetholic acid.* — Obtained, together with sugar, by boiling turpethin or turpethic acid with acids, in the same manner as jalapinolic acid is obtained from jalapin (xvi, 401). It is purified by washing and melting it with water, dissolving in weak alcohol, decolorising with animal charcoal, and crystallising three or four times from dilute alcohol.

White mass, consisting of microscopic needles and tufts. Melts at about 88°. Inodorous; tastes harsh. Has an acid reaction.

| | | | | | | Spirgatis. mean. |
|---|---|---|---|---|---|---|
| 32 C | ........ | 192 | ........ | 66·67 | ........ | 66·53 |
| 32 H | ........ | 32 | ........ | 11·11 | ........ | 11·21 |
| 8 O | ........ | 64 | ........ | 22·22 | ........ | 22·26 |
| $C^{32}H^{32}O^8$ | ........ | 288 | ........ | 100·00 | ........ | 100·00 |

Contains 2 at. water more than jalapinolic acid (xvi, 401).

Decomposes when heated, in the same manner as jalapinolic acid, emitting an extremely irritating odour, and leaving porous charcoal.

*Soda-salt.* — Dazzling-white, silky mass, appearing under the microscope as rhombic plates with angles of 558 and 125°.

| | | | | | | Spirgatis. |
|---|---|---|---|---|---|---|
| 32 C | ........ | 192 | ........ | 61·94 | ........ | 61·90 |
| 31 H | ........ | 31 | ........ | 10·00 | ........ | 9·99 |
| 7 O | ........ | 56 | ........ | 18·06 | ........ | 18·03 |
| NaO | ........ | 31 | ........ | 10·00 | ........ | 10·08 |
| $C^{32}H^{31}NaO^8$ | .... | 310 | ........ | 100·00 | ........ | 100·00 |

*Baryta-salt* — Amorphous.

| | | | | | | Spirgatis. |
|---|---|---|---|---|---|---|
| 32 C | ........ | 192 | ........ | 53·99 | ........ | 53·60 |
| 31 H | ........ | 31 | ........ | 8·72 | ........ | 8·75 |
| 7 O | ........ | 56 | ........ | 15·75 | ........ | 16·02 |
| BaO | ........ | 76·5 | ........ | 21·54 | ........ | 21·63 |
| $C^{32}H^{31}BaO^8$ | .... | 355·5 | ........ | 100·00 | ........ | 100·00 |

The acid dissolves easily in *alcohol*, less easily in *ether* (Spirgatis).

*Resin of Valerian root* (Trommsdorff, *Ann. Pharm.* x, 10, 222).

## E. Aldehyde-resin.

LIEBIG.   *Ann. Pharm.* 14, 158.
BLEY.   *N. Tr.* 25, 2, 79.
WEIDENBUSCH.   *Ann. Pharm.* 66, 152 ; *Pharm. Centr.* 1848, 852 ; *J. pr. Chem.* 46, 252 ; *Chem. Gaz.* 1849, 34 ; *Lieb. Kopp's Jahresber.* 1847 and 1848, 648.
FR. GÖTZ.   *N. Repert.* 12, 145.

*Formation.* 1. By heating aldehyde with caustic potash (viii, 278) (Liebig). The penetrating odour evolved in the reaction is due to the formation of a thick golden-yellow oil, having an odour of cinnamon and rapidly converted by oxidation in the air, or with nitric acid, into a resin different from aldehyde-resin (Weidenbusch).
— 2. By warming acetal (ix, 40) with alcoholic potash in presence of air (Liebig).

Döbereiner (*Schw.* 38, 327 ; 64, 466) previously noticed the formation of a resin on burning alcohol containing potash in his vinegar-lamp (viii, 207) : his oxygen-ether (viii, 274) is likewise oxidised by potash, and more quickly by oil of vitriol, to an indifferent yellow resin, soluble in alcohol and ether, and bleaching in sunlight. — Wood-spirit and fusel-oil, in contact with platinum, air, and potash, also form resins, though more slowly than alcohol (Götz).

The brown colour developed in alcoholic potash on standing, or on evaporating the solution in air, is due to the aldehyde-resin formed (Liebig). On boiling an alcoholic solution of soda and saturating it with an acid, a brown resin is obtained, soluble in alkalis and of varying composition. The same solution heated in sealed tubes yields a red resin insoluble in alkalis. A body having the same composition as the last is obtained also from wood-spirit : it contains, on the average, 74·88 p. c. C., 8·74 H., and 16·38 O., and may be represented by the formula $C^{12}H^8O^2$ (calc. 75·0 p. c. C., 8·33 H., and 16·67 O.). It is probably formed from 3 atoms of aldehyde by the elimination of 4 at. water. Formic acid is also produced in the reaction ; but if a little acetate or formiate of soda is added to the alcoholic soda, the resin produced contains 82·31 p. c. C. and 8·69 H. (Mylius, *Chem. News*, 1865, 148 ; *Zeitschrift Ch. Pharm.* 8, 526).

When aldehyde is heated to 160° in a sealed tube for 100 hours, a resin free from oxygen is formed, together with water, alcohol, and acetic acid. The resin contains 4 atoms of carbon to 2 atoms of hydrogen (Berthelot, *Compt. rend.* 56, 703 ; *Ann. Pharm.* 128, 256).

*Preparation.* 1. Aldehyde (Weidenbusch), or the liquid rich in aldehyde obtained by distilling alcohol with sulphuric acid and oxide of manganese (viii, 276, 3) (Liebig) is heated with solution of caustic potash, and the resin thereby produced is washed with water ; the smell of volatile oil, however, is not completely removed even by washing with boiling water (Weidenbusch). On precipitating the resin from its solution in caustic potash with dilute sulphuric acid, boiling the filtered solution in warm alcohol, after addition of water, to expel the alcohol, and drying the precipitated resin at 100° in a vacuum (see analysis *b*) it is no longer soluble in water and but incompletely soluble in alcohol (Liebig).
— 2. Solution of caustic potash of sp. gr. 1·26 is introduced, together

with some platinum-black, into a vessel filled with vapour of alcohol, which is opened from time to time. The potash quickly assumes a yellow colour, and deposits a dark-brown granular resin, which must be washed with as little exposure to the air as possible. Thus obtained, it contains about 9 p. c. of a resin soluble in alcohol, which is probably a product of oxidation, and may be removed by washing with alcohol (Götz).

Bley distils a mixture of 1 part of nitric acid of sp. gr. 1·24 and 4 parts of alcohol, and after rectifying the distillate over chloride of calcium, mixes it with caustic potash, so long as a yellow precipitate is produced. He then washes the precipitate with water, dissolves it in ether, and evaporates the solution. This aldehyde-resin is brittle, pale-brown, and easily fusible : it is decomposed by nitric acid, blackened by oil of vitriol, and is soluble in warm hydrochloric and acetic acids, and precipitable from the latter solution by water. It dissolves very slightly in warm aqueous ammonia and potash ; in cold absolute alcohol, but in alcohol of 80 p. c. only on warming ; and rapidly in ether and acetate of ethyl, as well as in warm oil of turpentine and oil of almonds.

*Properties.* Dark-brown, hard resin, triturable to a pomegranate-yellow [pale-brown (Liebig)] powder (Weidenbusch). Red, friable mass, resembling dragon's blood, turning paler and at last fawn-coloured in the air (Götz). Tasteless.

| | Liebig. | | Weidenbusch. | Götz. | |
| --- | --- | --- | --- | --- | --- |
| | *a.* | *b.* at 100° | *a.* | *a.* over oil of vitrol. | *b.* in vacuo. |
| C .... | 65·68 | 73·34 | 76·40 | 65·62 | 53·21 |
| H .... | 7·08 | 7·76 | 7·97 | 7·99 | 7·53 |
| O .... | 27·24 | 18·90 | 15·63 | 26·39 | 39·26 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

Liebig supposes *a* to contain potash. — Götz gives for the resin *a*, which is insoluble in alcohol, the formula $C^{32}H^{24}O^{10}$ : *b* is the portion soluble in alcohol and precipitable as a lemon-yellow powder by ether and chloroform ; Götz assigns to it the formula $C^{36}H^{30}O^{20}$.

Aldehyde-resin, dried at a moderate heat in the *air* and afterwards at 100°, exhales a spirituous odour and sometimes takes fire and burns like tinder. — When strongly *heated* it burns like a resin, leaving a shining charcoal (Liebig). — The brown alcoholic solution is decolorised by a little *chlorine*, whereupon water throws down a white powder containing chlorine (Weidenbusch). — Neither the resin insoluble in alcohol nor that soluble therein is decomposed by fused alkalis (Gotz).

Aldehyde-resin gradually dissolves when washed with *water*, forming a dark-brown solution. It is insoluble in *bisulphide of carbon* (Götz), partially soluble in *oil of vitriol*, from which it is precipitated by water, and nearly insoluble in *alkalis* (Weidenbusch). See above.

The resin prepared according to 1 dissolves easily in *alcohol* and *ether* (Liebig ; Weidenbusch) ; that prepared according to 2 is insoluble in alcohol, ether, and *chloroform* (Götz).

SECOND APPENDIX TO COMPOUNDS CONTAINING 40 ATOMS OF CARBON.

## Humous Substances.

VAUQUELIN.   *Ann. Chim.* 21, 29 ; *Crell. Ann.* 1798, 1, 424.
KLAPROTH.   *A. Gehl.* 4, 329.
TH. SAUSSURE.   *A. Gehl.* 4, 684.
EINHOF.   *A. Gehl.* 6, 381.
PROUST.   *J. Phys.* 63, 320 ; *N. Gehl.* 3, 374.
BRACONNOT.   *Ann. Chim.* 61, 187 ; *N. Gehl.* 9, 132. — *Ann. Chim.* 80, 289. — *Ann. Chim. Phys.* 12, 189 ; *Schw.* 27, 344 ; *Gilb.* 63, 365. — *Ann. Chim. Phys.* 31, 40.
BERZELIUS.   *Thoms. Ann.* 2, 314. — *Scher. Ann.* 7, 224. — *Pogg.* 13, 84. — *Pogg.* 29, 3, and 238.
SPRENGEL.   *Kastn. Arch.* 7, 163 ; 8, 145.
BOULLAY.   *J. Pharm.* 16, 165.
MALAGUTI.   *Ann. Chim. Phys.* 59, 313 ; *J. Pharm.* 21, 443.
HERMANN.   *J. pr. Chem.* 12, 277 ; 22, 65 ; 23, 375 ; 25, 189 ; 27, 165 ; 34, 156.
PELIGOT.   *Ann. Chim. Phys.* 67, 157 ; 73, 208 ; abstr. *J. pr. Chem.* 18, 188.
MULDER.   *J. pr. Chem.* 16, 246 ; 21, 203, and 331 ; 32, 325.
P. THENARD.   *Compt. rend.* 44, 980 ; 49, 289 ; 52, 444 ; *Par. Soc. Bull.* 1861, 33, and 60. — *Compt. rend.* 52, 792, 53, 1019.

The uncrystallisable brown or black substances produced by the decay of many organic compounds, more especially of vegetable tissues, and resembling the bodies formed by the action of acids or alkalis on sugar and woody fibre, are distinguished by the general name *humus, humous substance, mould,* or *peat-substance* (*Torfmaterie*), which terms include a large number of bodies having a similar external appearance. They are distinguished from crenic acid by the easy solubility in water of the latter body, which, however, is converted into insoluble apo-crenic acid by exposure to the air.   The composition of these bodies being seldom known, and their formulæ not determined with certainty, they are here treated in succession.

*Formation and Sources.*   I.  Humus is formed by the decay of many organic compounds, more particularly of vegetable tissues, and consequently occurs :

1.  *In Vegetable Soil.*   Concerning the formation of humus in the soil see Soubeiran (*N. J. Pharm.* 17, 321 ; *J. pr. Chem.* 50, 291 ; *Lieb. Kopp's Jahresber.* 1850, 651); Blondeau (*Compt. rend.* 57, 414 ; *Chem. Centr.* 1864, 252).   An aqueous extract of the cultivated soil of Versailles contained a substance allied to sugar or dextrin (Verdeil & Risler, *Compt. rend.* 35, 95 ; *Lieb. Kopp's Jahresber.* 1852, 786).   See also Risler (*N. Arch. ph. nat.* 1, 305 ; *Kopp's Jahresber.* 1858, 507).

2.  *In Stable manure:*   Thénard's fumic acid, Braconnot's azulmic acid, different from the azulmic acid of this Handbook (xi, 375).

3.  *In rotten wood* (Berzelius ; Hermann). — The black-brown pulve-

rulent residue of an oak-trunk which had rotted in a marsh, contained crenic acid, which it gave up to carbonate of ammonia, and an acid closely allied to apocrenic acid, but more completely precipitable by hydrochloric acid and insoluble in nitric acid (Berzelius, *Pogg.* 29, 262). — A deal pump-pipe, which had remained for a long time out of water, contained in the inner of the wood a large quantity of crenic acid, and in the outer layers principally apocrenic acid (Winckler, *Jahrb. pr. Pharm.* 20, 10; *Lieb. Kopp's Jahresber.* 1850, 392). See also A. Vogel (*N. Repert.* 6, 102).

4. In peat, of which it forms the chief part, together with undecomposed woody fibre (Einhof; Proust; Braconnot). In bituminous wood (Jameson, *Scher. J.* 7, 419; Braconnot). In lignite.

Concerning crenic acid and humous substances from peat (see Reinsch (*J. pr. Chem.* 24, 274); on the humic acid of peat : Wackenroder (*J. pr. Chem.* 24, 22); Soubeiran (*N. J. Pharm.* 18, 16). On humus from lignite, see Reinsch (*J. pr. Chem* 19, 478).

A black humus-like substance, probably rotten peat, found floating on the water of Loch Dochart, in Scotland, after the occurrence of an earthquake, contained 76·7 p. c. C., 4·7 H., and 18·6 O., besides traces of ash and nitrogen (Gregory, *Ann. Pharm.* 61, 365; *Lieb. Kopp's Jahresber.* 1847 and 1848, 808). — Haidinger's *dopplerite* is an earthy substance, occurring in a peat-bed at Aussee in Styria. In the fresh state it is gelatinous and brown-black, but on exposure to the air it becomes elastic and caoutchouc-like, and contains vegetable fibres, distinguishable under the microscope. After drying at 100°, whereby 78·5 p. c. of water is expelled, it has a glassy lustre, resembles pitch, and contains (after deducting ash and 1·03 p.c. of nitrogen) 51·63 p. c. C., 5·34 H., and 43·03 O., corresponding to the formula $C^{40}H^{25}O^{25}$. Caustic potash is without action upon it after drying, but with the fresh substance it evolves ammonia, and dissolves a portion, which is precipitated again by hydrochloric acid (Schrötter, *Wien Akad. Ber.* 1849, 285; *Lieb. Kopp's Jahresber.* 1849, 781). — *Pigotite*, a brown mass found in layers on the granite cliffs on the east and west coasts of Cornwall, probably formed from the remains of plants, contains Johnston's *mudesous acid* in combination with alumina. The acid is dark-brown, soluble, not deliquescent, and is represented by the formula $C^{12}H^{6}O^{8}$. Its silver-salt contains, in addition, 3 at. AgO.; the alumina-salt 4 at. $Al^{2}O^{3}$, and 8 at. HO. Chlorine converts it into white gelatinous *mudesic acid* $C^{12}H^{6}O^{10}$. Nitric acid forms the same acid as a brown deliquescent mass (Johnston, *Phil. Mag.* Nov. 1840; *J. pr. Chem.* 22, 182).

5. In the bark of many trees, especially in that of *Pinus sylvestris* (xv, 487); in cinchona-barks (xvi, 484) (Berzelius); in the bark of *Salix fragilis*, and abundantly in the bark of the beech (Braconnot), and in that of the oak and horse-chesnut (Thomson).

An aqueous decoction of anacahuita-wood yields with neutral acetate of lead, a precipitate of lead oxide combined with tannic and humic acids, the latter of which separates on dissolving the precipitate in acetic acid. When purified by washing, dissolving in aqueous ammonia, and precipitating with hydrochloric acid, it contains, after drying at 110°, 45·11 p. c. C., 4·56 H., and 50·33 O., corresponding to the formula $C^{16}H^{10}O^{14}$ (Ludw. Müller, *Pharm. Viertelj.* 10, 532).

From the alkaline excrescences of unhealthy trees, more especially of the elm, there exudes a black mass, Klaproth's *ulmin*, which

Smithson (*J. Phys.* 78, 311) recognised as a compound of a humous substance with potash.

On mould of blighted corn, see Gräger (*Ann. Pharm.* 8, 67); Lucas (*Ann. Pharm.* 37, 90); from *Sphœria deusta*, Knop (*Pharm. Centr.* 1851, 648). A brown substance from *Mucor septicus* also belongs to this place (Braconnot, *Ann. Chim.* 80, 289).

II. By imperfect carbonisation or combustion, as well as by the dry distillation of wood and other organic substances: humus, consequently, occurs in soot (Braconnot). See xv, 159. — Charcoal prepared at a low temperature for making gunpowder, contains ulmic acid (Boullay).

III. Many spring waters especially those rising in peat-bogs, as well as the ochre which is deposited from them, contain soluble humous substances, which are rendered insoluble by exposure to the air : Berzelius's *crenic* and *apocrenic acids*.

The water of the Seine yields with sesquichloride of iron (not in excess) a precipitate, from which caustic potash extracts an acid resembling apocrenic acid, and containing 53·1 p. c. C., 2·7 H., 2·4 N., and 41·8 O. (Peligot, *Bull de la Soc. d'Encouraq.* (1864) 63, 542.

An acid occurring in the mineral water of Ronneburg agrees in many respects with crenic acid, but its compounds with potash and soda, when exposed to the air in the moist state, take up oxygen, and are converted into apocrenates and nitrates (Döbereiner, *J. pr. Chem.* 1, 113). Concerning Hänle's *Brunnensäure*, which differs from crenic acid, see *Kastn. Arch.* 8, 399 ; on the crenic acid of the Moldau water, see Pleischl (*N. Br. Arch.* 17, 81) ; on crenic acid in rain-water see Salm-Horstmar (*Pogg.* 54, 254).

IV. Limonite and earthy vivianite, clay iron-stone, pea-ore, also sand and ferruginous clay contain small quantities of humus (Wiezmann, *Kastn. Arch.* 12, 442). On the compound of humus with ferric oxide, see Nöggerath & Mohr, *Ann. Pharm.* 25, 93). An oolitic red iron-stone from Belgium contained 4 per cent. of crenate of ammonia (Phipson, *Compt. rend.* 52, 975 ; *Kopp's Jahresber.* 1861, 976).

V. Human urine contains a humous substance, which dissolves easily in aqueous potash, and is precipitable by acids as a curdy black mass, insoluble in water and alcohol (Proust, *Ann. Chim Phys.* 14, 264). Prout's *melanic acid* (*Phil. Ann.* 4, 71 ; *Schw.* 36, 188), precipitated from unhealthy dark-coloured human urine by acids, appears to be identical with the last. A humus-like substance from the excrement of the nightingale also belongs to this place (Braconnot, *Ann. Chim. Phys.* 17, 386).

When horses' urine is precipitated by hydrochloric acid, and caustic potash is added to the filtrate, a precipitate of brown flocks is thrown down, which, after washing, gives up a large quantity of magnesia to warm hydrochloric acid. After being freed from hydrochloric acid by washing, and dried, it forms a brown-black powder, which dissolves very slightly in water and in hydrochloric and nitric acids, easily in caustic alkalis and their carbonates, also in alcohol, and is precipitated from the alkaline solutions by magnesia-salts. The urine of all graminivorous animals, and guano, contain a similar substance (v. Bibra, *Ann. Pharm.* 53, 199).

VI. By the action of alkalis on woody fibre, with access of air (Braconnot); of alkalis on dextro-glucose (or inverted sugar); of acids on cane-sugar (Malaguti ; Boullay). See xv, 318.

Wood-charcoal made at a temperature of 320° is converted by melted hydrate of potash, with access of air, and more slowly by aqueous carbonate of potash, into an acid humous substance, which dissolves in ammonia and aqueous alkalis (Millon, *Compt rend.* 51, 249; *Kopp's Jahresber.* 1860, 68).

VII. The products formed by treating charcoal with nitric acid very closely resemble crenic and apocrenic acids (Berzelius).

VIII. The brown residue, insoluble in acids and water, which remains when cast-iron is dissolved in nitric acid, behaves towards ammonia in the same manner as the ferric salt of apocrenic acid, but it cannot be obtained in the pure state (Berzelius). See v. 216; xi, 375.

IX. When a mixture of carbonate of soda and phosphorus is heated to 240° for some hours in a glass tube, a dark-brown mass is formed, which, when thrown into water, evolves a large quantity of spontaneously inflammable phosphoretted hydrogen, and yields a brown solution containing phosphate and carbonate of soda together with humous substance. The latter body is precipitated from the brown filtrate by hydrochloric acid, washed with water containing hydrochloric acid till it begins to dissolve more freely; again dissolved in dilute caustic soda, and precipitated by hydrochloric acid. — It is amorphous and black-brown, and has a conchoïdal fracture, resinous lustre, and slightly acid reaction. It contains 44·7 p. c. of ash and 15 p. c. of phosphoric acid, and in 100 parts of the organic substance forming the remainder, 63·88 C., 4·00 H., and 32·12 O., corresponding approximately to the formula $C^{40}H^{16}O^{16}$. Its aqueous solution is precipitated by most salts (Dragendorff, *Chem. Centr.* 1861, 865).

X. The compound of carbonic oxide and potassium formed in the preparation of potassium, when dissolved in water and freed as far as possible from crystallisable salts by evaporating the solution, yields with dilute sulphuric acid a brown humus-like precipitate. This body dissolves with difficulty in cold, more freely in hot water, and in weak alcohol, but not in absolute alcohol or ether. Its solutions are dark-brown or black, and opaque, and are completely precipitated by acids, including acetic acid. It dissolves easily in alkalis, and is precipitated by metallic salts. The copper-compound, obtained by mixing its solution in weak alcohol with sulphate of copper, contains at 100°, on the average, 45·49 p. c. C., 2·45 H., 2·76 N., 19·11 CaO., and 30·19 O., corresponding to the formula $C^{38}NH^{12}O^{16},3CuO$ (W. Mayer. *In Gmelin's Manuscripts*).

Certain decomposition-products of gallic acid (xii, 401) and tannic acid (xv, 458); the carbonaceous mass obtained by treating alcohol with oil of vitriol (viii, 240); the substances produced by the action of hydrochloric acid on albumin (see *Albumin*) are all distinguished as humous substances.

On the humus-like products formed by heating chloride of carbon with alcoholic potash, see Berthelot (*N. Ann. Chim. Phys.* 54, 87; *Ann. Pharm.* 109, 121): on similar substances resulting from the action of sodium on chloroform, in presence of wood-spirit, alcohol, acetone, &c., see Hardy (*Compt. rend.* 54, 470; *Chem. Centr.* 1862, 672. — *Par. Soc. Bull.* 1863, 339).

## Humous Substances in particular.

### A. *Boullay's Ulmic Acid.*

Boullay (*J. Pharm.* 16, 165 ; *Schw.* 60, 107 ; *Pogg.* 20, 63) distinguishes as ulmic acid the brown substance produced by the action of acids on cane-sugar (xv, 256), besides many other bodies evidently not belonging to this place. Ulmic acid (the source and mode of preparation of which is not given) is said to contain 56·5 p. c. C., 4·81 H., and 38·69 O. ; the copper-salt, dried at 120° in a vacuum, 10·5 p. c. CuO. ; the lead-salt 26·86 p. c. PbO. ; the silver-salt 28·57 AgO. ; the two latter salts, however, were partially decomposed by washing.

### B. *Substances produced by the action of Acids on Cane Sugar.*

Malaguti's *ulmin* is obtained by boiling cane-sugar with very dilute acid (xv, 254) ; it is freed from ulmic acid, produced at the same time, by ammonia, or better by caustic potash, after which the insoluble portion is washed with water, very dilute sulphuric acid, and water, in succession. It contains, on the average, 56·89 p. c. C., 4·72 H., and 38·39 O., corresponding to the formula $C^{24}H^{12}O^{12}$ (57·14 p. c. C., 475 H.).

Malaguti's *ulmic acid* is formed exclusively when the flocks formed are removed from the further action of the acid. It is obtained, together with a little ulmin, by boiling 10 parts of sugar, 30 parts of water, and 1 part of oil of vitriol, and repeatedly removing the scum which is formed. After drying at 150° it contains 56·98 p. c. C., 4·76 H., and 37·76 O., and is, therefore, isomeric with ulmin, into which it is transformed by boiling with water for a few hours. It dissolves in ammonia and caustic potash. The copper-salt contains 10·76 p. c. CuO. ; the silver-salt 24·32 p. c. of silver (Malaguti, *Ann. Chim. Phys.* 59, 413).

According to Mulder, the coloured substances, insoluble in acidulated water, produced by boiling cane-sugar with hydrochloric or sulphuric acid, are either brown ulmin-substances containing 2 atoms of hydrogen more than the number of oxygen-atoms, or black humin-substances containing equal numbers of atoms of oxygen and hydrogen. The ulmin of the former and the humin of the latter class are insoluble in aqueous alkalis, whilst ulmic and humic acids are soluble therein ; ulmin and humin, however, are converted by alkalis into the corresponding acids ; and ulmin-substances are transformed by the action of dilute acids, with access of oxygen, into humin-substances, and ulmic acid by strong acids into ulmin. — If the sugar has already been converted by dilute acids into glucic acid, strong acid forms exclusively humin (Mulder, *J. pr. Chem.* 21, 203 and 354 ; 32, 331).

Mulder gives the following formulæ :—ulmin, $C^{40}H^{16}O^{14}$ ; ulmic acid, $C^{40}H^{14}O^{12}$ ; humin, $C^{40}H^{16}O^{15}$ ; humic acid, $C^{40}H^{12}O^{12}$. These formulæ, as well as the entire distinction between ulmin- and humin-substances, appear to me untenable. Mulder, it is true, refers to many points of difference between the two classes of bodies, in colour,

behaviour towards acids, acetates, &c. ; but to all appearance, it is not these differences, but trifling variations in the analyses (probably of substances containing ash) that determine whether a body belongs to the ulmin or to the humin group. The formulæ of these bodies appear to be derivable from that of sugar by the abstraction of water (Kr.).

Calculation for Mulder's Ulmin and Humin substances from sugar.

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 24 C | ........ | 145 | .... | 64·16 | 24 C | ........ | 145 | .... | 66·82 | 24 C ........ 145 .... 69·71 |
| 9 H | ........ | 9 | .... | 3·98 | 8 H | ........ | 8 | .... | 3·69 | 7 H ........ 7 .... 3·36 |
| 9 O | ........ | 72 | .... | 31·86 | 8 O | ........ | 64 | .... | 29·49 | 7 O ........ 56 .... 26·93 |

$C^{24}H^9O^9$ .... 226 .... 100·00    $C^{24}H^8O^8$ .... 217 .... 100·00    $C^{24}H^7O^7$ .... 208 .... 100·00

C = 6·04, as in Mulder's analyses of these bodies.

1. When 12 parts of sugar, 40 parts of water, and 1 part of hydrochloric acid are heated to 80° for a sufficient length of time, brown flocks are obtained, which are collected, washed, and dried at 165°. They contain 65·3 p. c. C., 4·3 H., and 30·4 O., and are, according to Mulder, a mixture of ulmin and ulmic acid. — They are partially soluble in ammonia.

1 a. The flocks obtained in 1 are rendered insoluble in ammonia by digestion in hydrochloric acid, the ulmic acid, according to Mulder, being converted into ulmin. The body, dried at 140°, now contains 65·11 p. c. C., 4·32 H., and 30·57 O., from which numbers Mulder calculates the formula $C^{40}H^{16}O^{14}$.

2. Ten parts of sugar are boiled with 30 parts of water and 1 part of oil of vitriol, and the product is dried at 165°. It contains 64·72 p. c. C., 4·50 H., and 30·78 O., and is, according to Mulder, a mixture of ulmin and ulmic acid not perfectly dry. — It is partially soluble in ammonia and caustic potash.

2 a. The portion of 2 soluble in caustic potash, when precipitated by sulphuric acid, dried, triturated, and digested with dilute hydrochloric acid to remove potash, is ulmic acid, containing, at 195°, 68·95 p. c. C., 4·23 H., and 26·82 O. According to Mulder $C^{40}H^{14}O^{12}$.

2 b. The portion of 2 soluble in aqueous ammonia, when washed with hydrochloric acid and water, is ulmin. After drying at 140° (at which temperature the air-dried substance loses 9·2 p. c. of water) it contains 65·45 p. c. C., 4·47 H., and 30·08 O., and is represented by the formula $C^{40}H^{16}O^{14}$ (Mulder).

3. Four parts of sugar are boiled with 1 part of strong hydrochloric acid and 10 parts of water (apparently with excess of air), and the product is washed and dried at 165°. It contains 65·36 p. c. C., 4·38 H., and 30·26 O., and consists, according to Mulder, of a mixture of ulmin and humic acid. — It is insoluble, for the most part, in ammonia.

3 a. The portion of 3 insoluble in ammonia, after washing with dilute hydrochloric acid and drying at 160° (whereby water containing acetic acid is expelled), contains 66·71 p. c. C., 4·40 H., and 28·89 O. = $C^{40}H^{14}O^{12} + 1\frac{1}{2}$ HO : Mulder's ulmin.

4. Ten parts of sugar are boiled with 20 parts of water and 2 parts of oil of vitriol. A portion of the product is black and insoluble in

caustic potash, and contains, at 140°, 64·67 p. c. C., 4·32 H., and 31·01 O.: Mulder's humin, $C^{40}H^{15}O^5$. A second portion is soluble in caustic potash, from which it is precipitated as a brown-black jelly by acids, and contains, at 140°, 63·25 to 64·01 p. c. C., 4·61 to 4·38 H., and 32·14 to 31·61 O. $= C^{40}H^{17}O^{15}$.

A portion of the jelly is soluble in ammonia. The reddish insoluble residue contains, at 140°, 65·66 p. c C., 4·26 H., and 30·08 O., corresponding to the formula $C^{40}H^{16}O^{14}$.

The above substances are capable of yielding salts and double salts.

*Ammonia-salt.* By treating 2 with aqueous ammonia, evaporating the filtrate, and drying the product at 140°, the ammonia-salt of *ulmic acid* is obtained. It contains 64·84 p. c. C., 3·97 N., 5·06 H., and 26·13 O., corresponding to the formula $C^{40}H^{14}O^{12},NH^4O$. The ammonia-salt of *humic acid* is obtained by treating 3 in a similar manner. It contains 64·94 p. c. C. and 4·53 H., agreeing with the formula $C^{40}H^{12}O^{12},NH^4O$.

*Potash-salt.* — Obtained by dissolving ulmic acid in caustic potash, evaporating the neutral solution, and drying the residue at 140°. Contains 12·31 p. c. KO., corresponding to the formula $C^{40}H^{14}O^{12},KO$.

*Baryta-salt.* — Prepared by neutralising the potash-salt with acetic acid and precipitating with chloride of barium. It cannot be washed. Dried at 140°, it contains 13·59 p. c. BaO., agreeing with the formula $3C^{40}H^{14}O^{12},2BaO$.

*Copper-salt.* — Obtained from sulphate of copper in the same manner as the baryta-salt. When dried at 140°, it contains 10·20 p. c. CuO., corresponding to the formula $C^{40}H^{14}O^{12},CuO$.

*Lead-salt.* — Prepared from neutral acetate of lead in the same manner as the baryta-salt. At 140° it contains 31·02 p. c. PbO, and is represented by the formula $3C^{40}H^{14}O^{12},4PbO$.

*Ammonio-plumbic salt.* — Neutral acetate of lead throws down from the ammonia-salt of ulmic acid, an ammoniacal precipitate containing, at 140°, 55·03 p. c. C., 3·74 H., and 17·76 PbO.

*Silver-salt.* — Nitrate of silver throws down from the ammonia-salt of humic acid, a precipitate free from ammonia, which, after drying at 100°, loses 6·83 p. c. of water at 140°. The salt dried at 100° contains 49·05 p. c. C., 3·23 H., 24·58 O., and 23·14 AgO, and corresponds to the formula $C^{40}H^{15}O^{15},AgO$.

*Ammonio-argentic salt.* — Precipitated by nitrate of silver from an ammoniacal solution of 1 or 2. Dark-brown and contains ammonia. Dried at 140° it contains 57·09 to 57·89 p. c. C., 3·61 to 3·90 H., 1·59 N., 23·19 O., and 14·52 to 13·59 AgO., and is, according to Mulder, a salt of ulmic acid represented by the formula $2C^{40}H^{14}O^{12},NH^4O,AgO$.

*Decomposition-products of Humin-substances from Sugar.* — a. *By the action of Chlorine.* Ulmin, ulmic acid, humin, and humic acid, when subjected to the prolonged action of chlorine in presence of water,

yield one and the same substance, Mulder's *chlorohumic acid*. This body is formed rapidly with alkaline ulmic acid, more slowly with humic acid suspended in water, and only after 20 to 40 hours when humin is employed. — It forms an inodorous pale-red or brick-red jelly, triturable to an orange-yellow powder. When dried at 120° it has the composition *a*, and at 155° the composition *b*.

> *a.* 50·53 p. c. C., 3·30 H., 35·96 O., 9·87 Cl = $C^{32}ClH^{13}O^{17}$.
> *b.* 53·41 p. c. C., 3·49 H., 32·36 O., 10·74 Cl = $C^{32}ClH^{12}O^{16}$.

The former acid was prepared from the potash-salt of ulmic acid, the latter from the ammonia-salt of humic acid.

The acid dissolves when washed with water. It dissolves easily in ammonia-water and caustic potash, also in alcohol, but not in ether. — Its baryta-salt, obtained by double decomposition, contains, after slight washing and drying at 118°, 43·09 p. c. C., 3·04 H., 29·98 O., 8·64 Cl., and 15·25 BaO., corresponding to the formula $C^{32}ClH^{13}O^{17}$,BaO (Mulder).

*b. By the action of Nitric acid.* When digested with strong nitric acid, humin and ulmin substances become hot, turn red, and give off a large quantity of formic acid. When heated with nitric acid diluted with more than an equal weight of water, they turn red and afterwards dissolve, and at length yield formic and oxalic acids.

The red substance produced by the action of strong nitric acid contains 53·71 p. c. C., 3·44 H., 5·02 N., and 37·83 O. The body formed with dilute acid is Mulder's *humin-nitric acid*, afterwards regarded as identical with apocrenate of ammonia. After once washing, pressing, and drying (whereby acid water is expelled) it forms a rust-red powder. It dissolves in water and in alcohol, but not in ether: it is soluble also in oil of vitriol, and in aqueous ammonia, potash, and soda, with blood-red colour, ammonia being evolved by the action of potash. Its metallic salts are brown jellies.

The *acid* contains, at 120°, 55·43 p. c. C., 2·98 N., 3·49 H., and 38·10 O., corresponding to the formula $C^{48}NH^{18}O^{26}$; the *ammonia-salt*, obtained by dissolving the acid in ammonia and evaporating, contains, at 120°, 51·67 p. c. C. and 4·33 H. = $C^{48}NH^{16}O^{24}$,2NH$^4$O : the *silver-salt*, at 115°, 30·31 p. c. AgO.; the *lead-salt* precipitated from the potash-salt by neutral acetate of lead, at 110°, 28·97 p. c. C., 1·80 N., 1·88 H., 22·67 O., and 44·68 PbO., corresponding to the formula $C^{48}NH^{18}O^{26}$, 4PbO (Mulder).

*c. By the action of Oil of Vitriol.* When ulmin or ulmic acid is mixed with oil of vitriol and the black pasty mass is diluted, after some hours, with a large quantity of water, a hard black powder, partially soluble in ammonia, is obtained. It contains, at 1·55°, 64·35 p. c. C., 4·17 H., and 31·48 O., corresponding to the formula $C^{40}H^{15}O^{16}$ (Mulder), or $C^{24}H^9O^9$ (Kr.).

*d. By the action of Caustic Potash.* — *α.* The blood-red solution of humin and humic acid in very strong caustic potash, when heated to incipient fusion in a silver vessel, and mixed, after cooling, with sulphuric acid, yields a black precipitate, which is not decomposed by chlorine, and is dissolved with difficulty by nitric acid, forming a red solution. When dried at 145° it contains 70·83 p. c. C., 4·62 H., and 24·55 O., agreeing with the formula $C^{34}H^{13}O^9$ (Mulder).

$\beta$. If the potash-solution is heated for a longer time, till hydrogen begins to be evolved and carbonic acid formed, nearly the whole of the dissolved body is thrown down as a black mass, which, after washing and drying at 140°, contains 77·70 p. c. C., 4·07 H., and 18·23 O. = $C^{34}H^{10}O^6$ (Mulder).

$\gamma$. Lastly, if the fusion is continued so long as the alkali continues to froth up, and until a faint glowing is perceptible, with empyreumatic odour, the black insoluble powder contains, at 150°, 86·84 p. c. C., 3·18 H., and 9·98 O., corresponding to the formula $C^{34}H^7O^3$ (Mulder).

### C.  *Products formed by the Action of Potash on Vegetable Fibre.*

*Peligot's Ulmic Acid.*

Braconnot heats sawdust, paper, or linen with an equal quantity of hydrate of potash and a little water in a silver crucible, till the mass becomes soft and the sawdust dissolves with frothing; then cools the product, dilutes with water, and precipitates the filtrate with sulphuric acid. The brown flocks still contain about 4 per cent. of ash. They dissolve in ammonia and in alcohol.

When woody fibre purified as much as possible is heated with half its weight of hydrate of potash and a little water, with constant stirring, till the mass becomes soft, but not until the fibres are completely dissolved, acids throw down from the filtrate a yellow precipitate, which melts in boiling water, and contains, at 100°, 64·57 to 66·3 p. c. C., and 6·2 to 6·3 H. (Peligot).

When the mixture is heated more strongly and for a longer time, with a larger proportion of potash, a black precipitate, Peligot's ulmic acid, is obtained. It contains at 120°, on the average, 70·7 p. c. C., 6·1 H., and 23·2 O., corresponding to the formula $C^{27}H^{14}O^6$ (Peligot). Probably $C^{24}H^{12}O^6$ (70·59 C., 5·88 H) (Kr.).

The potash-salt, prepared from hydrate of potash and excess of ulmic acid, contains, after evaporation in a vacuum and drying at 120°, 16·8 p. c. KO. — The silver-salt, precipitated from the ammonia-salt by nitrate of silver, contains 31·4 p. c. of silver (Peligot).

### D.  *Crenic Acid.*

BERZELIUS.  *Pogg.* 29, 3, and 238; *Lehrbuch.* 3, *Aufl.* 8, 393.

*Quellsäure.  Humusquellsäure.  Krensäure.*

*Source.*  In many springs, especially abundant in the Porla spring in Oerebro Län (Sweden), and in the ochre deposited therefrom. — In ochre from the soil of Lisma; in a bog-ore from Smaland; in a white mealy earth, consisting chiefly of silica, from Degernä.

On the occurrence of crenic acid in rotten wood, see below.

*Preparation.  From the ochrey deposit of the Porla Spring.*  The finely powdered deposit is boiled with caustic potash, till it assumes the flocculent appearance of precipitated sesquioxide of iron; it is then

filtered and washed, and the filtrate is supersaturated with so much acetic acid, that on adding acetate of copper, a brown (not a green) precipitate is produced; and the apocrenic acid is thrown down by the addition of acetate of copper. After neutralising the filtrate with carbonate of ammonia and heating it to 50° till the supernatant liquid appears of a pure blue colour, the crenic acid is precipitated as copper-salt, which is washed and decomposed under water by hydrosulphuric acid. The liquid can be filtered from sulphide of copper only after standing 24 hours in a stoppered vessel, after which the pale-yellow filtrate is evaporated in a vacuum. There remains a dark-yellow fissured mass, containing, besides crenic acid, the compounds of the acid with lime, magnesia, and manganese. This mass is treated with absolute alcohol, which dissolves crenic acid and a little crenate of magnesia; the alcoholic solution is rapidly evaporated in a vacuum; the yellowish-brown residue is dissolved in water, and mixed with small portions of neutral acetate of lead, so long as brown apocrenate of lead is produced, and until the precipitate produced by a drop of the acetate either re-dissolves, or appears of a greyish-yellow colour only; and the liquid is filtered and precipitated by basic acetate of lead. The precipitate thus obtained is well washed and decomposed by hydrosulphuric acid, and the filtrate is evaporated in a vacuum.

*Properties.* Pale-yellow transparent mass, becoming yellow and opaque on prolonged drying. Tastes sharply and distinctly acid; a strong solution is styptic, a dilute solution tasteless. Reddens litmus.

*Decompositions.* The *aqueous,* and still more the *alcoholic* solution turns dark in the air, and leaves a brownish residue. When submitted to dry distillation, the acid softens, swells up, emits fumes, and yields a yellow acid distillate, containing ammonia and a thick yellowish-brown oil, leaving charcoal. — When heated with *nitric acid,* it evolves a little nitric oxide, and on evaporating the liquid, there remains a yellowish mass, which still behaves towards alkalis and acetate of copper like crenic acid. — The acid in combination with *alkalis* undergoes alteration in the air like gallic acid, becoming brown and passing into apocrenic acid.

The acid dissolves in all proportions in *water*. Its concentrated solution is syrupy. — It dissolves without alteration in cold *nitric acid*.

The *salts* of crenic acid are amorphous. The acid expels acetic acid from the acetates. — The crenates of the alkalis are easily alterable in the air. Their concentrated aqueous solutions resemble vegetable extracts. The salts of the alkaline earths are less easily soluble; those of the metals are, for the most part, sparingly soluble precipitates, dissolving more or less on washing. — The acid forms neutral and acid salts.

*Ammonia-salt.*—Becomes acid on evaporation, and leaves a brown, extract-like mass, still containing a large quantity of ammonia.

*Potash-salt.* — Prepared by dropping a solution of the acid in absolute alcohol into acetate of potash, also dissolved in absolute alcohol. — Nearly white precipitate, yellow and horny after drying. Neutral. Dissolves in alcohol of sp. gr. 0·86.

The *soda-salt* behaves like the potash-salt; the *baryta-salt* like the lime-salt.

*Lime-salt.* — *Neutral.* — Pale-yellow flocks, obtained by precipitating chloride of calcium with excess of the potash-salt. It dissolves in a larger quantity of water, and remains on evaporation as a yellow transparent varnish, which is often white and earthy within. — With excess of crenic acid, it forms an acid salt insoluble in alcohol, and with lime-water pale-yellow flocks of a basic salt. — On neutralising crenic acid as completely as possible with hydrate of lime, evaporating the solution in a vacuum, boiling the yellow transparent residue a few times with alcohol, and drying at 100°, there remains a lime-salt containing 20·59 p. c. of lime.

The *magnesia-salt* is easily soluble in water; the acid salt slightly soluble in absolute alcohol.

*Alumina-salt.* — Aqueous crenic acid and moist hydrate of alumina yield a yellow insoluble compound, or with a larger proportion of acid a soluble compound. The latter body is not precipitated by ammonia, and even after evaporation therewith is perfectly soluble in water.

*Silicic acid* precipitated from a liquid containing crenic acid takes up a portion of the acid, which is only partially extracted from it by potash.

*Lead-salts.* — Basic acetate of lead throws down from crenates of the alkalis a yellowish white basic salt. — The precipitate produced by neutral acetate of lead in aqueous crenic acid redissolves at first: on continuing to add the neutral acetate so long as (owing to the presence of apocrenic acid) a brown or dark-yellow precipitate is produced, then filtering, dropping the filtrate into neutral acetate of lead, washing the precipitate thereby formed with alcohol, and drying it in a vacuum and afterwards at 100°, a neutral salt is obtained, containing 51·2 p. c. of oxide of lead.

*Ferrous salt.* The aqueous acid dissolves iron, forming a soluble acid salt, which oxidises in the air.

*Ferric salt.* Aqueous crenic acid produces in ferric salts free from acid, dark streaks, which quickly disappear, after which a pale reddish-grey, almost white precipitate is produced. After drying, the precipitate is earthy, and of a dirty white colour. It dissolves completely in ammonia, and remains on evaporation as a reddish-yellow residue, from which water dissolves a neutral double salt, leaving a basic salt behind. — It is decomposed, without being dissolved, by caustic alkalis and their carbonates.

*Copper-salt.* — Crenic acid precipitates acetate of copper completely at 50° only; the crenates of the alkalis also precipitate sulphate of copper. The precipitate is dirty-white when first thrown down, but soon turns greenish-grey. It dissolves slightly in water and easily in acetic and crenic acids. The solution in acetic acid leaves on evaporation a red residue containing suboxide of copper.

The *mercurous* salt is insoluble, the *mercuric* salt soluble.

*Silver-salt.* Crenic acid scarcely renders nitrate of silver turbid at first, but after a time it produces a whitish-grey precipitate, which gradually assumes a dark-purple colour. The precipitate forms a

colourless solution with nitric acid and a pale-yellow solution with ammonia. — A crenate of an alkali with a small quantity of nitrate of silver remains clear, on account of the formation of a double salt, but with a larger quantity of the nitrate, crenate of silver is thrown down.

Crenic acid dissolves in all proportions in absolute *alcohol*. If it contains salts of crenic acid, it becomes opaque before the alcohol extracts the acid.

### E. *Apocrenic Acid.*

BERZELIUS. *Pogg.* 29, 3, and 238.

*Quellsatzsäure.*

Occurs in the water of the Porla spring and in other waters, being produced by the action of the air on crenic acid.

*Preparation.* The precipitate of apocrenate of copper obtained in the preparation of crenic acid (p. 466) is washed a few times with water, which it still colours yellow, since the precipitate is more soluble in pure water than in saline solutions. It is then decomposed under water by hydrosulphuric acid; the sulphide of copper is allowed to subside; the dark-brown liquid is evaporated; and the residue is exhausted with absolute alcohol, whereby salts are left behind and two different modifications of apocrenic acid are dissolved, according to the quantity of alcohol employed. An additional quantity of the acid may be obtained from the sulphide of copper.

*a.* A small quantity of alcohol takes up from the above residue, apocrenic acid, which is black-brown and fissured after drying, and triturable to a dark-red powder. It reddens litmus, has a styptic taste, dissolves with brown colour in water, and is partially precipitated in flocks by acids and by sal-ammoniac.

*b.* The undissolved portion of the residue, when warmed with more alcohol, gradually dissolves with brown colour, and remains on evaporation similar in appearance to *a.* It reddens litmus, has less taste than *a*, and becomes paler and soft in water, without dissolving.

*c.* A modification of apocrenic acid, likewise sparingly soluble in water, is extracted from the sulphide of copper by aqueous acetate of potash. On evaporating the solution, it is obtained as apocrenate of potash and is freed from admixed acetate by means of alcohol of sp. gr. 0·86. Hydrochloric acid precipitates the acid, though incompletely, from a solution of the potash-salt.

The acid prepared according to *a*, and that prepared according to *b* and *c*, are distinguished by the following behaviour. When precipitated from their solutions by hydrochloric acid, re-dissolved in caustic potash, and mixed with freshly precipitated hydrate of alumina, the latter body acquires a dark colour, and precipitates *b* and *c* completely, but in the case of *a*, a salt of crenic acid remains in solution, and may be precipitated by acetate of copper. According to Berzelius, this crenic acid was not merely an admixture, but formed, in combination with a second body, the apocrenic acid *a*.

Apocrenic acid dissolves in cold *nitric acid* of sp. gr. 1·25, forming

a solution which loses its colour when heated, with evolution of a little nitric oxide, and leaves on evaporation an acid pale-yellow mass behaving like crenic acid.

It expels acetic acid from its salts, forming *apocrenates*. Its salts are amorphous, black-brown, and generally less easily soluble in water than the crenates. The soluble salts are precipitated by acids, with the exception of acetic acid.

*Ammonia-salt.* — On dissolving 100 parts of the acid dried at 100° in aqueous ammonia, and evaporating the solution, there remain 113·22 parts of ammonia-salt dried at 100°. This salt has an acid reaction, and is soluble in water. When dried at 100° in a current of air, it gives off ammonia and becomes partly insoluble in water.

*Potash-salt.* — A solution of the acid in acetate of potash gives off acetic acid when evaporated, and leaves a neutral residue from which alcohol takes up the remaining acetate of potash. — The apocrenate forms a black, fissured, easily pulverisable mass, soluble in water with brown colour, and completely precipitable from the solution by alcohol.

The *soda-salt* resembles the potash-salt. — The *baryta-* and *lime-salts* are black-brown precipitates, which gradually dissolve on washing with water. The basic salts are quite insoluble.

*Alumina-salt.* A small quantity of hydrate of alumina dissolves in aqueous apocrenic acid : a larger quantity throws down the acid from its solution in water or alkalis, in the form of a black-brown precipitate, which when obtained from alkaline solution, leaves potash and alumina on ignition, and is insoluble in ammonia.

The *lead-salt* contains, at 100°, 45·25 p. c. of oxide of lead.

*Ferrous salt.* — The neutral salt is soluble in water. By exposure to the air, it is converted into basic ferric salt. — The basic ferrous salt, precipitated from the potash-salt mixed with a little ammonia by proto-salts of iron, is a black precipitate, turning brown in the air, like the ochre of the Porla spring.

*Ferric salt.* The acid and its potash-salt throw down from ferric sulphate, black flocks which dissolve with black colour in ammonia. On evaporating the solution, there remains a black extract, from which water takes up a neutral double salt, whilst a basic ferric salt remains undissolved. — The salt dissolves in caustic potash and then deposits a basic salt, whilst apocrenate of potash remains in solution, together with a little sesquioxide of iron, which may be removed by hydrosulphuric acid.

*Cupric salt.* Acetate of copper mixed with acetic acid, throws down from aqueous apocrenic acid, an acid salt, in the form of a brown, gummy precipitate, which dissolves slightly, with dark colour, in water. From this solution a little alkali precipitates the neutral salt.

Apocrenic acid does not precipitate solutions of *gelatin*, even on addition of hydrochloric acid.

Analyses of Crenic and Apocrenic acids of unknown origin, by Hermann
(*J. pr. Chem.* 12, 284).

|   |      | Crenic acid. |             | Apocrenic acid. |
|---|------|--------------|-------------|-----------------|
| C | .... | 39·49        | ............ | 61·4            |
| N | .... | 7·50         | ............ | 15·0            |
| H | .... | 7·69         | ............ | 4·8             |
| O | .... | 45·32        | ............ | 18·8            |
|   |      | 100·00       | ............ | 100·0           |

Hermann's nitrogen determinations seem to be all wrong (Kr.).

## F. *Substances derived from Peat, Rotten Wood, and Vegetable Mould.*

*From Peat. Sprengel's Humic Acid.*—Pulverised peat is treated with
hydrochloric acid to remove salifiable bases, and the residue is digested
with aqueous ammonia for some days in a stoppered vessel. The
ammoniacal solution thus obtained is diluted, filtered, and precipitated
by hydrochloric acid, and left at rest, in order that the hydro-
chloric acid may dissolve as much as possible of the bases from the
precipitated humic acid. The precipitate is then washed and dissolved
in aqueous carbonate of soda, and the solution is filtered (whereby
sesquioxide of iron and alumina are removed), and precipitated with
excess of hydrochloric acid. After standing for 24 hours, the liquid
is decanted, and the precipitate washed with hot and cold water in
succession, the wash-waters acquiring a deeper colour the more com-
pletely the hydrochloric acid is removed (Sprengel). —

Shining, black, jet-like mass, breaking up into irregular fragments,
which exhibit a conchoïdal fracture. Very hygroscopic. Tastes sour
and styptic in the moist state. Reddens litmus (Sprengel), according to
Berzelius and Einhof, on account of adhering acid.

When submitted to *dry distillation*, it yields gases, acetic acid, and
empyreumatic oil, leaving a hard, dense charcoal. — *Burns* with flame.
— *Chlorine* decolorises the water in which humic acid is suspended,
throwing down a white resin. — *Nitric acid* forms artificial tannin; *oil
of vitriol* carbonises it on heating. — In the moist state it absorbs
oxygen.

Freshly precipitated humic acid dissolves slightly in cold, and more
freely in hot *water*. When the solution is frozen, the dissolved portion
is thrown down. The acid is likewise rendered insoluble by perfect
drying. — The brown solution in *oil of vitriol* is precipitated by
water.

Humic acid forms *salts* with bases. It expels carbonic acid from
alkaline carbonates, and forms precipitates of acid humates with
solutions of earthy and metallic salts. The humates of the alkali-
metals yield by double decomposition with metallic salts, sometimes
neutral, sometimes basic compounds. The insoluble salts, when freshly
precipitated, form brown or black slippery masses, which contract very
much on drying, and break up into black shining particles. The salts
insoluble in water dissolve for the most part in aqueous alkalis,
especially in ammonia, and partly also in aqueous alkaline carbonates
which, however, decompose some of the other salts. See particulars
about the salts in the original memoirs (p. 458.).

Humic acid dissolves in hot *acetic acid*, and in *alcohol* before drying, but not afterwards (Sprengel).

*From Peat, Rotten Wood, Vegetable Mould* (Mulder, *J. pr. Chem.* 21, 321).

a. *From Peat.* — When peat is washed with water and alcohol to remove soluble matters and resins, and the residue is boiled with carbonate of soda, a dark solution is obtained, from which acids throw down a brown or black jelly, the liquid still remaining of a dark colour. The jelly dissolves in washing, as soon as the wash-water becomes free from acid. By this treatment, black peat from the Haarlem lake yielded humic acid, whilst light brown Friesland peat yielded ulmic acid.

The *humic acid* contains 7·5 p.c. of ash, and likewise ammonia, which cannot be completely separated, but is partly expelled at 140°. When dried at 140°, it contains 60·13 p.c. C., 4·74 H., 3·61 N., and 31·52 O., and according to Mulder, is represented by the formula $C^{40}H^{12}O^{12},NH^3 + 4HO$.

The *ulmic acid* contains 1·4 p.c. of ash, but is free from ammonia. Its ammonia-salt is obtained by dissolving it in ammonia, evaporating the solution, and drying the residue at 140°. The acid, dried at 140°, contains 62·02 p.c. C., 4·65 H., and 33·33 O., corresponding to the formula $C^{40}H^{18}O^{16}$. The ammonia-salt contains, at 140°, 61·20 p.c. C., and 4·91 H., corresponding to the formula $C^{40}H^{14}O^{12},NH^3 + 3HO$.

b. *From the rotten wood of Salix alba.* — Obtained in the same manner as *a*. Contains ammonia, and 1·9 p.c. of ash. Dried at 140°, it contains 59·09 p.c. C., 4·97 H., 2·80 N., and 33·18 O., agreeing with the formula of the ammonia-salt of humic acid, $C^{40}H^{12}O^{12},NH^3 + 5HO$ (Mulder). By again dissolving the substance in caustic potash and precipitating with sulphuric acid, a precipitate is obtained, containing, at 140°, 62·50 p.c. C., 4·88 H., and also ammonia.

c. From *Vegetable Mould.* Obtained by washing the mould with boiling water, boiling it with carbonate of soda, precipitating the solution with hydrochloric acid, washing the gelatinous precipitate with water, drying, and boiling with alcohol, to remove crenic and apocrenic acids. The jellies thus obtained still contain ammonia and varying proportions of ash, amounting in some cases to 27 per cent. According to Mulder, they are in most cases to be regarded as humic acid, $C^{40}H^{12}O^{12}$, with ammonia and water.

Humous substances from Vegetable Mould.

| | 1. | | 2. | | 3. | | 4. | | 5. |
|---|---|---|---|---|---|---|---|---|---|
| C .... | 57·45 | ........ | 61·90 | ........ | 57·54 | ........ | 60·04 | ........ | 56·91 |
| N .... | 3·25 | ........ | | ........ | | ........ | 3·31 | ........ | 6·11 |
| H .... | 4·52 | ........ | 4·65 | ........ | 4·71 | ........ | 4·66 | ........ | 5·31 |
| O .... | 34·90 | ........ | | ........ | | ........ | 31·99 | ........ | 31·67 |
| | 99·12 | ........ | | ........ | | ........ | 100·00 | ........ | 100·00 |

| | 6. | | 7. | | 8. | | 9. | | 10. |
|---|---|---|---|---|---|---|---|---|---|
| C .... | 58·44 | ........ | 59·09 | ........ | 57·87 | ........ | 55·18 | ........ | 60·94 |
| N .... | | ........ | 3·63 | ........ | 3·52 | ........ | 2·35 | | |
| H .... | 5·27 | ........ | 5·12 | ........ | 4·98 | ........ | 5·00 | ........ | 4·85 |
| O .... | | ........ | 32·16 | ........ | 33·63 | ........ | 37·47 | | |
| | | | 100·00 | ........ | 100·00 | ........ | 100·00 | | |

2 was obtained by dissolving 1 in caustic potash and precipitating with acids. 4 was prepared from 3 by digesting it in hydrochloric acid, boiling with alcohol, and collecting the undissolved portion. 5 and 6 are the same substance, 5 being dried at 140°, and 6 at 195°. Boiling water took up a large proportion of 9, and left 10 undissolved.

Mulder's *crenic* and *apocrenic acids* are obtained from tilled soil, and according to Hermann, are identical with his humocrenic and torfocrenic acids; the former is, according to Mulder himself, identical with humin-nitric acid, and also with Stas's phloretin (xvi, 8). — To obtain these bodies the soil is boiled with water, and with carbonate of soda in succession; the latter solution is precipitated with dilute sulphuric acid, and filtered from the humin thereby thrown down; and the filtrate is mixed, first with caustic potash, then with acetic acid to slightly acid reaction, and lastly with acetate of copper, which throws down apocrenic acid. The filtrate, neutralised with carbonate of ammonia, yields a precipitate of crenic acid in combination with oxide of copper, which is purified by dissolving it in acetic acid, and precipitating with alcohol.

The apocrenate of copper contains ammonia, on which account Mulder regards it as a double salt, and assigns to the acid the formula $C^{48}H^{12}O^{24}$. Dried at 140°, it contains 42·8 to 47·1 p. c. CaO., the organic part containing 51·39 p. c. C., 3·91 H., 3·73 N., and 40·97 O. When decomposed by hydrosulphuric acid, it yields apocrenic acid.

The crenate of copper contains phosphate of copper, and generally also ammonia. On one occasion, after having been purified by repeatedly dissolving it in acetic acid, and precipitating with alcohol, it was obtained almost free from nitrogen, and contained 60·17 p. c. of oxide of copper. The organic part contained, in 100 parts, 46·87 C., 4·97 H., and 48·16 O., corresponding to the formula $C^{24}H^{12}O^{16} + 3HO$ (Mulder, *J. pr. Chem.* 32, 321).

*Humous acids of Russian black earth* (*Tschornosem*) (Hermann, *J. pr. Chem.* 12, 277).

*a.* From the solution obtained with carbonate of soda, sulphuric acid throws down *a* in brown flocks.

*b.* On exhausting untilled black earth with hydrochloric acid, and afterwards with carbonate of soda, and precipitating the latter solution with hydrochloric acid, the substance *b* is obtained. Similar treatment of earth cultivated for many years, yields the body *c.*

All three acids may be resolved into crenic, apocrenic, and humic acids, in different proportions.

|   |   | a. |   | b. |   | c. |
|---|---|---|---|---|---|---|
| C | .... | 56·73 | ........ | 59·68 | ........ | 60·83 |
| N | .... | 13·69 | ........ | 8·02 | ........ | 11·05 |
| H | .... | 5·34 | ........ | 4·12 | ........ | 4·31 |
| O | .... | 24·24 | ........ | 28·18 | ........ | 23·81 |
|   |   | 100·00 | ........ | 100·00 | ........ | 100·00 |

Hermann (*J. pr. Chem.* 22, 65; 23, 375; 25, 189; 27, 165; 34, 156) distinguishes eleven different humous substances, most of which he regards as nitrogenous, even when they are obtained from substances free from nitrogen, as in the case of bodies prepared from cane-sugar, according to xv, 255, the nitrogen being absorbed from the air. (See also xv, 157.) They are as follows :—

I. Substances insoluble in acetate of soda, soluble in alkalis, and precipitable from the solutions by mineral acids. — Humic acids in the more restricted sense.

1. *Anitrohumic acid.* — The substance formed, according to Malaguti (xv. 275), by the action of sulphuric acid on sugar in the absence of air; Malaguti's ulmic acid.

2. *Saccharo-humic acid.* — The acid produced in a similar manner to the last, but with access of air. It contains 6·88 p. c. of nitrogen, and in the copper-salt 10·8 p. c. CuO.

3. *Ligno-humic acid.* — Obtained from pale-brown rotten wood by boiling it with aqueous carbonate of potash, which dissolves humous extract and ligno-humic acid, and leaves nitrolin undissolved. From the solution the ligno-humic acid alone is precipitated by hydrochloric acid in the form of a brown jelly. Dried at 100° it contains 57·23 p. c. C., 6·47 N., and 5·22 H.; and in the copper-salt, 5·1 p. c. CuO.

4. *Metaligno-humic acid.* — Formed by boiling freshly precipitated ligno-humic acid with water, by which it loses its sliminess, becoming pulverulent, and altering its capacity of saturation. The acid contains at 100°, 56·94 p. c. C., 6·77 N., and 5·00 H.: the copper-salt 7·04 p. c. CuO.

II. Substances soluble in alkalis and acetate of soda, and precipitable by mineral acids. — Hermann's apocrenic acids. Berzelius's apocrenic acid belongs to this place, but is found to differ from the substances 5 and 6.

5. *Torfic acid.* — Obtained from Russian peat by boiling it with carbonate of soda, supersaturating the solution with acetic acid, precipitating with acetate of copper, dissolving the precipitate in caustic potash, and precipitating with hydrochloric acid. This precipitate, dissolved in a strong solution of acetate of soda, and evaporated nearly to dryness, deposits a little humic acid, whilst torfic acid remains in solution, and may be precipitated by acetate of copper and separated as above. — In alkaline solution it absorbs oxygen. The salts of the alkalis are soluble and dark-brown: the remaining salts are basic, neutral, or acid, generally insoluble, but soluble in caustic alkalis and their carbonates, if the base consists of lime, alumina, oxide of iron, or oxide of copper. The acid dried at 100° contains 61·92 p. c. C., 7·73 N., and 4·31 H.: the neutral potash-salt contains 14·7 p. c. KO.; the acid soda-salt 5·27 NaO; the lime-salts 8·5 to 13·55 CaO.; the copper-salt 9·58 to 13 p. c. CuO.

6. *Tula and Siberian Arvic acid (Tula-und Siberische Ackersäure).* — Obtained from tilled soil in the same way as 5. Differs from 5 only in the percentage of nitrogen, which varies from 4·89 to 15·00 per cent.

III. Substances soluble in water. This class includes Berzelius's crenic acid.

7. *Humus-extract.* — Occurs in tilled soil, peat, and rotten wood; also in soot, wood-tar, and pyroligneous acid. (See xv, 151.) — When rotten wood is boiled with carbonate of soda, and the filtrate is supersaturated with nitric acid, a precipitate of ligno-humic acid is thrown down, whilst humus-extract remains in solution. The latter body is precipitated by the addition of nitrate of lead and ammonia, and the

precipitate is washed, agitated with dilute sulphuric acid not in excess, and exhausted with alcohol. On evaporating the alcoholic solution, the humus is left as a brown transparent varnish, containing, at 100°, according to the analysis of the lead-compound, 56·68 p. c. C., 4·56 H., and 4·50 N. It yields by dry distillation an empyreumatic liquid holding humus-extract in solution. — Dissolves easily in water, with the exception of an insoluble portion produced during evaporation. From the concentrated, but not from dilute solutions, various acids and salts throw down the extract as a brown resinous precipitate. The compounds with baryta and lime are sparingly soluble: the latter compound is formed by boiling rotten wood or garden mould with lime, and separates in the form of brown pellicles on the surface of the liquid on evaporation. The extract prevents the precipitation of sesquioxide of iron and other metallic salts by ammonia: it is not precipitated from its solutions by neutral metallic salts, or by ammoniacal acetate of copper, and is thereby distinguished from crenic acid. The precipitate produced by basic acetate of lead is of a light colour in the moist state, but brown after drying: it contains 40 p. c. PbO. The precipitate thrown down by ammoniacal sulphate of copper contains at 110°, 35·00 p. c. CuO., 15·77 HO., and 49·23 of humus extract. — The extract dissolves easily in alcohol.

8. *Humocrenic acid.* — Occurs in Black earth. The solution of lignocrenic acid in excess of alkali absorbs oxygen and nitrogen, according to Hermann, and forms with nitric acid a precipitate of " Torfsatzsäure," together with humo-crenic acid, which is thrown down from the filtrate by ammonia and basic acetate of lead. The lead-salt forms yellowish flocks, containing, at 100°, 76·62 p. c. PbO., the remainder containing 52·01 p. c. C., 4·47 H., and 6·60 N. The copper-salt is grey-green, and contains, at 100°, 50 p. c. CuO., the organic portion containing 46·71 p. c. C., 5·01 H., and 6·11 N.

9. *Torfocrenic acid.* — Occurs in peat, in black earth, and in the mineral water of Moskau. It is slowly produced by the action of the air on alkaline " Torfsatzsäure," and is separated from the solution in the same way as 8. It forms lead-salts containing 62·0 to 82·5 p. c. of lead-oxide, the organic part containing 42·05 p. c. C., 5·30 H., and 6·25 N. The copper-salt contains 58·0 p. c. CuO., the remainder containing 33·91 p. c. C., 6·34 H., and 5·12 N.

10. *Torfoxycrenic acid.* — Occurs, together with 8, in the Moskau mineral water. The water is evaporated to $\frac{1}{10}$th of its volume and filtered, and the filtrate is acidified with acetic acid and precipitated, at 60°, with acetate of copper, which throws down torfoxycrenate of copper, whilst *torfocrenic acid*, precipitable by ammonia, remains dissolved in the filtrate. — The lead-salt contains 73·5 p. c. PbO., and in the residue 60·54 p. c. C., 2·43 H., and 11·6 N.; the copper-salt contains 60 p. c. CuO., the organic portion containing 41·21 p. c. C., 4·63 H., and 8·28 N.

IV. Substances insoluble in acids and alkalis.

11. *Nitrolin.* — The principal constituent of rotten wood, remaining behind when the wood is washed and boiled with water and carbonate of soda. It is brown, and still shows the structure of the wood, and becomes horny on drying. Contains, at 100°, 56·13 p. c. C., 6·32 H., and 13·20 N., or more frequently only 4 p. c. N.

G. *Substances obtained from Lignite. Herz's Carbo-ulmic and Carbo-*
*humic acids.*

When powdered lignite (from the coal of the Hohenpeissenberg in Southern Bavaria) is boiled with alcohol to remove resin, and afterwards subjected to prolonged boiling with strong caustic soda, and the deep-brown liquid thereby formed is filtered and precipitated with hydrochloric acid, dark-brown flocks are obtained, from which alcohol takes up carbo-ulmic acid, leaving carbo-humic acid undissolved.

Carbo-ulmic acid contains, on the average, 62·36 p. c. C., 4·77 H., and 32·87 O., corresponding with the formula $C^{40}H^{18}O^{16}$: the silver-salt contains 50·79 p. c. AgO.

Carbo-humic acid contains, at 130—140°, 64·59 p. c. C.. 5·15 H., and 30·26 O.; the silver-salt 25·21 p. c. AgO. (Herz, *N. Repert.* 10, 496).

## H. *Substances obtained from Dung.*

*Braconnot's Azulmic acid.* — When decomposed stable manure is exhausted with water, a residue containing ulmic acid is left, whilst the aqueous solution contains azulmic acid precipitable by acids. The latter acid is also obtained by evaporating the aqueous extract to a syrup, mixing it with alcohol of 32° B., decanting the slightly coloured alcohol, and decomposing the precipitated black mass with acids. — It forms a black, brittle mass, having a jet-like lustre, and leaving a yellowish-brown ash when burnt, and carbon free from nitrogen when carbonised. It dissolves in ammonia and alkalis, but not in alcohol (Braconnot, *N. Ann. Chim. Phys.* 12, 212).

P. Thénard's *Fumic acid* (*acide fumique, Düngersäure*) is also precipitated by acids from the aqueous solution of fermented dung; Thénard, however, purifies it by boiling the precipitate with the liquid, which causes it to cohere, washing, dissolving it ten times in ammonia-water, and precipitating with acids, so that at last the wash-waters remain colourless. It forms an amorphous black mass, having a shining fracture, and containing $\frac{1}{10}$th per cent. of ash, and 60·5 p. c. C., 5·1 H., 5·5 N., and 28·9 O., besides sulphur. According to Thénard, it is represented by the formula $C^{30}NH^{15}O^{11}$. It forms decomposition-products with chlorine and nitric acid, and is rendered soluble by exposing its ammonia-salt to the air, especially together with clay, or by the action of ozone, whereby nitric acid is formed, or when its lime-salt is boiled for 14 days with carbonate of lime, sesquioxide of iron, and water, whereby the oxide of iron is reduced if air is excluded, or alternately reduced and oxidised if air is admitted. The acid forms soluble salts with ammonia and the alkalis, and insoluble salts with the other bases: its ammonia-salt, however, precipitates salts of alumina only after addition of chloride of sodium, and does not precipitate phosphate of alumina even in presence of excess of ammonia. Thénard regarded as identical with this fumic acid, a brown nitrogenous product which he obtained by heating dextro-glucose with ammonia (xv, 318) or with nitrate of baryta (xv, 319), or by heating cellulose, milk-sugar, and cane-sugar with phosphate of ammonia (Thénard).

# COMPOUNDS CONTAINING 42 ATOMS OF CARBON.

*Primary Nucleus* $C^{42}H^{14}$.

## Idryl.

$C^{42}H^{14}$.

C. Bödeker. *Ann. Pharm.* 52, 100; *J. pr. Chem.* 33, 249.

Occurs in *Stupp*, a black mass mixed with globules of mercury, obtained in an experimental distillation of mercury in closed vessels from a mercurial mineral found in Idria (*Idrialite*).

Stupp is boiled repeatedly with alcohol, and the solution, after cooling, is separated from the yellow laminæ of a hydrocarbon different from idryl, which is deposited, and freed from the greater part of the alcohol by distillation, whereupon a brownish-black oil collects at the bottom of the vessel. This oil is boiled repeatedly with acetic acid so long as it continues to take up idryl and deposit it from the golden-yellow solution in needles on cooling. The needles are washed with acetic acid and with water, and recrystallised from alcohol, the laminæ which are first deposited from the strong solution on cooling, and consist of the hydrocarbon differing from idryl, being removed.

*Properties.* Loose crystalline mass of needles, collecting in nodules when slowly evaporated. Under the microscope rhombic laminæ are discernible. The crystals are nearly colourless, with a tinge of yellowish-green, and form a colourless powder when triturated. Melts at 86° to a clear pale-yellow oil, which solidifies to a radiated crystallised mass. Sublimes easily in very delicate laminæ. Has a faint, somewhat smoky odour, and no particular taste, but produces a slight burning sensation on the tongue.

|  |  |  |  |  | Bödeker. mean. |
|---|---|---|---|---|---|
| 42 C | 252 | ........ | 94·73 | ........ | 94·57 |
| 14 H | 14 | ........ | 5·27 | ........ | 5·46 |
| $C^{42}H^{14}$ | 266 | ........ | 100·00 | ........ | 100·03 |

Isomeric or polymeric with chrysene (xv, 1).

Idryl assumes a golden-yellow colour in cold *oil of vitriol*, and dissolves freely therein at 100°, forming a deep greenish-yellow liquid not precipitable by water; sulphurous acid is not given off till the liquid is strongly heated.

Idryl dissolves slightly in *acetic acid, alcohol, ether,* and *oil of turpentine* in the cold, and very freely when warmed, the last three solutions when saturated at the boiling heat, becoming solid on cooling. A very small quantity of idryl dissolved in these liquids produces a fine bluish iridescence, similar to that of a solution of sulphate of quinine.

The *hydrocarbon obtained in the preparation of idryl* forms delicate laminæ, which melt above 100° only, and sublime in fine colourless laminæ before melting completely. It contains 93·65 p. c. C., and 5·67 H. It dissolves in oil of vitriol, with brown-red colour, when warmed, and is somewhat less easily soluble than idryl in acetic acid and alcohol.

*Appendix to Idryl.*

## Idrialin.

DUMAS.  *Ann. Chim. Phys.* 50, 193 ; *Ann. Pharm.* 5, 16 ; *Schw.* 66, 83 ; *N. Tr.* 26, 1, 212.
SCHRÖTTER.  *Baumgärtner's Zeitschr. für Phys.* &c., 3, 245.
LAURENT.  *Ann. Chim. Phys.* 59, 385 ; 66, 143.
BÖDEKER.  *Ann. Pharm.* 52, 100.

Occurs in idrialite from Idria, which consists almost entirely of this substance. See Schrötter (*Baumgärtner's Zeitschr.* 4, 5). First noticed by Hacquet in 1778.

*Preparation.* 1. The pulverised mineral is slowly sublimed in a current of carbonic acid, the temperature being ultimately allowed to rise till the glass softens. The melted mass yields successively mercury and idrialin, which are collected and separated by treatment with boiling oil of turpentine (Dumas). — 2. The finely powdered idrialite is boiled with 20 or 30 parts of oil of turpentine, which, after cooling and filtering from the deposited idrialin, is again poured upon the idrialite until the mineral is exhausted (Laurent). Bödeker decolorises the product with animal charcoal, recrystallises from acetone or from a mixture of alcohol and oil of turpentine, and washes the crystals with alcohol.

*Properties.* Very light colourless laminæ, having a pearly lustre.

|  |  |  |  |  |  | Laurent. |  |  |  | Bödeker. |
|---|---|---|---|---|---|---|---|---|---|---|
| 42 C | 252 | ........ | 91·97 | ........ | 91·85 | ........ | 91·64 | ....... | 92·11 |
| 14 H | 14 | ........ | 5·11 | ........ | 5·30 | ........ | 5·27 | ........ | 5·29 |
| O | 8 | ........ | 2·92 | ........ | 2·85 | ........ | 3·09 | ........ | 2·60 |
| C⁴²H¹⁴O | 274 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Dumas and Laurent considered idrialin to be free from oxygen. Gerhardt (*Traité* 4, 305) doubles the formula.

Idrialin does not melt without decomposition, and distils undecomposed in very small quantity only (Dumas). — It dissolves in warm *oil of vitriol* with indigo-blue colour, forming a conjugated sulphuric

acid, the potash-salt of which forms fine silvery crystals (Schrötter). The baryta- and lead-salts of the acid are likewise soluble (Bödeker). — Idrialin forms with *chlorine* a solid compound, soluble with purple colour in oil of vitriol (Schrötter). — Fuming nitric acid forms a dark-brown solution precipitable by water (Schrötter).

When idrialin is boiled with strong nitric acid, a red powder, Laurent's *nitrite d'idrialase,* is obtained, which is insoluble in water, ether, and boiling alcohol, but dissolves partially, with brown colour, in caustic potash, and explodes on charcoal or when heated. It contains 62·67 p. c. C., 3·10 H., and 10·50 N., from which numbers Laurent calculates the formula $C^{20}X^2H^8$, and Gerhardt (*Traité,* 4, 306) the less probable formula $C^{84}X^5H^{23}O^2$ (65·2 p. c. C., 2·9 H., 9·0 N.).

Idrialin is insoluble in boiling *water,* and very slightly soluble in boiling *alcohol* and *ether,* but freely soluble in boiling *oil of turpentine,* from which it is deposited almost entirely on cooling (Dumas). Boiling *bisulphide of carbon, rock-oil,* and *oil of turpentine* dissolve idrialin very freely, but take up very little of it from the mineral containing it, except when heated above their boiling-points in closed vessels. *Linseed-oil, olive-oil,* and *crosote* dissolve the mineral almost entirely when heated therewith (Schrötter).

*Primary Nucleus* $C^{42}H^{26}$; *Oxyazo-nucleus* $C^{42}N^2H^{20}O^4$.

## Strychnine.

$$C^{40}N^2H^{22}O^4 = C^{42}N^2H^{20}O^4, H^2.$$
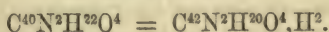
PELLETIER & CAVENTOU. *Ann. Chim. Phys.* 10, 142 ; *J. Pharm.* 5, 145 ; *N. Tr.* 3, 2, 224 ; *Repert.* 7, 169 ; *Berl. Jahrb.* 1820, 206 ; abstr. *Gilb.* 63, 287. — *Ann. Chim. Phys.* 26, 44 ; *Schw.* 42, 65 ; *Repert.* 18, 69.

PELLETIER & DUMAS. *Ann. Chim. Phys.* 24, 176.

MERCK. *N. Tr.* 20, 1, 134.

LIEBIG. *Pogg.* 21, 21 and 487. — *Ann. Pharm.* 26, 56.

DUFLOS. *Schw.* 62, 68.

REGNAULT. *Ann. Pharm.* 26, 17 ; *J. pr. Chem.* 16, 763. — *Ann. Pharm.* 29, 58.

PELLETIER. *Ann. Chim. Phys.* 63, 165 ; *Ann. Pharm.* 22, 114. — *J. Pharm.* 24, 154 ; *Ann. Pharm.* 29, 49 ; *J. pr. Chem.* 14, 180.

GERHARDT. *Ann. Pharm.* 42, 312. — *Compt. chim.* 1845, 116 ; *Rev. scient.* 10, 192. — *N. Ann. Chim. Phys.* 7, 251.

DITR. BRANDIS. *Ann. Pharm.* 66, 257 ; *Instit.* 1848, 194 ; *Pharm. Centr.* 1847, 952 ; *Lieb. Kopp's Jahresber.* 1847 and 1848, 627.

NICHOLSON & ABEL. *Chem. Soc. Qu. J.* 2, 241 ; *Ann. Pharm.* 71, 79 ; *Pharm. Centr.* 1849, 785 ; *N. Ann. Chim. Phys.* 27, 401 ; *N. J. Pharm.* 16, 305 ; *Lieb. Kopp's Jahresber.* 1849, 380.

HORSLEY. *Pharm. Journ.* 16, 177 ; *J. pr. Chem.* 72, 312 ; *Instit.* 1856, 463 ; *Lieb. Kopp's Jahresber.* 1856, 758.

SCHÜTZENBERGER. *Compt. rend.* 47, 79 and 235 ; *Instit.* 1858, 239 ; *J. pr. Chem.* 75, 122 ; *Ann. Pharm.* 108, 349 ; *Chem. Centr.* 1858, 677 ; *Kopp's Jahresber.* 1858, 373.

Discovered by Pelletier & Caventou in 1818. — Occurs [combined with igasuric acid (x, 229)? See also Marsson (*N. Br. Arch.* 55, 295)] in the *Nux vomica* of *Strychnos Nux vomica* (Handbuch viii. [2], 57), together with brucine and igasurine; in the *Faba St. Ignatii* of *Strychnos Ignatii*, together with a very small quantity of brucine; in very small quantity in *Lignum colubrinum* from *Strychnos colubrina* (Handbuch, viii [2], 56). — In the root-bark of *Strychnos Tieuté* and in *Upas Tieuté*, the Japanese arrow poison, together with traces of brucine (Pelletier & Caventou), whereas the North American arrow-poison contains curarin. Java arrow-poison, found in a bamboo, contained 62 p. c. of strychnine Frerichs, *Pharm. Viertelj.* 12, 542).

Concerning the quantities of brucine and strychnine present in pharmaceutical preparations of the above plants, see F. Mayer (*N. Jahrb. Pharm.* 23, 38; *Chem. Centr.* 1865, 320).

The base known as strychnine is, according to Schützenberger, a mixture of three different bases, having the formulæ C$^{40}$N$^2$H$^{22}$O$^4$, C$^{42}$N$^2$H$^{22}$O$^4$, and C$^{44}$N$^2$H$^{22}$O$^4$. The base with 42 atoms of carbon is said to be immediately deposited from dilute hydrochlorate of strychnine in long slender needles on addition of ammonia, whilst that with 40 atoms of carbon crystallises from the filtrate in octahedra after a quarter of an hour. These statements stand much in need of confirmation (Kr.).

*Preparation.* I. *From Nux vomica.* The nuts are either rasped or bruised: to render them fit for the latter operation, Milarch roasts them in an oven. Or they may be subjected to an atmosphere of steam for half an hour in a close vessel, and afterwards dried.

1. Nux vomica is boiled with water till it becomes soft: it is then bruised, returned to the boiling water, boiled for two hours, pressed, and again boiled twice. The liquid thus obtained is evaporated to a syrup and mixed with alcohol so long as gum is precipitated, the strychnine, brucine, colouring matter, and a little fat remaining in solution. The precipitate is washed with alcohol, and the alcoholic liquids are evaporated to an extract and diluted with cold water, whereby fat is thrown down. The filtrate is heated and decomposed with excess of milk of lime, which precipitates strychnine and brucine. The precipitate is pressed, dried, and boiled two or three times with 85 p. c. alcohol, which takes up strychnine, brucine, and colouring matter. The alcohol is distilled off and the residue digested with cold alcohol of 54 p. c., whereby brucine and colouring are dissolved, whilst strychnine remains behind, and is purified by crystallisation from boiling 85 p. c. alcohol [Corriol's process (*J. Pharm.* 11, 492; *N. Tr.* 12, 1, 173; abstr. *Mag. Pharm.* 13, 148) modified by Soubeiran, *N. J. Pharm.* 45, 230)].

2. Nux vomica is boiled with alcohol; the tincture is evaporated; and the extract is dissolved in water; the fat thereby separated is removed; the filtrate is boiled for a few minutes with a quantity of magnesia amounting to $\frac{1}{32}$nd of the nux vomica employed; and the greenish-yellow precipitate is collected. It contains chiefly strychnine, which is obtained by boiling it with alcohol of 38° B., evaporating the solution, and washing the resulting crystals with very cold alcohol of 22° B. The brucine is deposited from the filtrate from the magnesia precipitate after the lapse of a few days only (Pelletier & Caventou).

3. Rasped nux vomica is digested with five times its weight of 40 p. c. alcohol for a day, at a gentle heat. The liquid is strained through

linen, and the residue is pressed and treated twice again in the same
way. The whole of the tinctures are submitted to distillation and
further evaporated down to the weight of the nux vomica employed.
About $\frac{1}{50}$th of neutral acetate of lead is added; the liquid is filtered
from the precipitate, evaporated to one-half, mixed with $\frac{1}{50}$th of cal-
cined magnesia, and allowed to stand for a week, with frequent stirring.
The precipitate is then collected, washed, dried, and exhausted thrice ·
with hot 80 p. c. alcohol, which takes up strychnine, brucine, and
colouring matter. After distilling off the alcohol, the strychnine and
brucine are separated by means of 40 p. c. alcohol, as in 1 (Wittstein,
*Darstell. u. Prüfung*, 215). The processes of Wittstock (*Berzel. Lehrb.* 3 ed. 6,
296) and Winckler (*Mag. Pharm.* 19, 261) are similar to the foregoing. Pelletier &
Caventou had previously employed basic acetate of lead, for which Neuhaus (*N. Tr.*
11, 2, 198) substituted the neutral acetate.

See the methods of Duflos (*Berl. Jahrb.* 28, 2, 208. — *Schw.* 62, 69) and
O. Henry (*J. Pharm.* 16, 752; *Repert.* 37, 123), who extract with alcohol or water
containing sulphuric acid; also the similar method of Ferrari (*Brugn. Giorn.*
16, 457; abstr. *Schw.* 40, 492). N. E. Henry (*J. Pharm.* 8, 401; *N. Tr.* 7, 1,
336) and Robiquet extract with boiling water. — O. Henry (*J. Pharm.* 21, 222)
precipitates the bases with infusion of galls (vii, 177): Lebourdais and Tilloy
(*N. J. Pharm.* 23, 406) precipitate them with animal charcoal. See p. 266.

According to Wittstein, 213 parts, according to Pelletier & Caven-
tou, 354 parts of nux vomica yield 1 part of strychnine.


II. *From Ignatius' beans.* — 1. The rasped beans are first exhausted
with warm ether to remove fat, and then boiled repeatedly with alcohol.
The alcoholic liquid thus obtained is evaporated; the residue is boiled
with magnesia and water; and the precipitate thereby formed is washed
with cold water and boiled with alcohol, which, after filtering and eva-
porating, deposits the strychnine (Pelletier & Caventou). Or the beans
may at once be boiled with alcohol, and the fat separated by cooling the
liquid for some days (Steinmann. *Schw.* 25, 410). — 2. One part of the
beans is digested for a few days with 2 parts of 75 p. c. alcohol and
4 parts of water, the tincture is poured off, and the softened beans are
dried over a water-bath, pulverised (now an easy process), and exhausted
with a warm mixture of sulphuric acid, 2 parts of alcohol, and 4 parts
of water. The mixed tinctures are then precipitated with basic acetate
of lead, filtered, and freed from excess of lead by means of sulphuric
acid; the perfectly clear filtrate is evaporated down to the weight of
the beans employed; and the now brown and gelatinous liquid is
exhausted with warm alcohol. The tincture, mixed with water and
freed from alcohol by distillation, is precipitated with ammonia, and the
precipitate is purified by dissolving it in water containing sulphuric
acid, and, lastly, by crystallising it from hot alcohol (Geiseler, *N. Br.
Arch.* 2, 73).


III. *From Upas Tieuté.* — This substance is dissolved in water; the
filtrate is digested with magnesia; the reddish-yellow precipitate, after
washing and drying, is boiled three times with alcohol; and the reddish
tincture is evaporated. The strychnine thus obtained is coloured green
by nitric acid, on account of an admixture of strychnochromin (p. 505).
It is purified by dissolving it in dilute sulphuric acid, digesting with
animal charcoal, precipitating with magnesia, exhausting the precipi-
tate with alcohol, and evaporating (Pelletier & Caventou).

Strychnine containing brucine is purified by treating it with cold weak alcohol, which dissolves almost exclusively brucine, and re-crystallising from hot strong alcohol (Pelletier & Caventou). Cold absolute alcohol takes up the brucine, leaving strychnine undissolved. The two alkaloïds may also be separated by dissolving them in very weak nitric acid, not in excess, and evaporating the solution, whereupon the nitrate of strychnine first separates in white feathery crystals, the brucine-salt afterwards forming hard solid crystals. The greater part of the latter salt remains in the mother-liquor as a gummy mass, which is to be again treated with magnesia and alcohol (Wittstock; Pelletier & Dumas). — When a strongly acid solution of the two bases in acetic acid is mixed with chromate of potash, the strychnine alone is precipitated, and may be recovered from the precipitate by means of ammonia (Horsley). Strychnine containing brucine is reddened by moderately strong nitric acid: the pure alkaloïd behaves as described below.

*Detection of Strychnine in cases of poisoning.* — The substance to be examined is digested with very weak hydrochloric acid for an hour or two, at a temperature of 60° to 80°; the liquid is strained; and the residue is again exhausted with hot water containing hydrochloric acid. The extracts are then mixed with a slight excess of ammonia and evaporated to dryness, together with sand. The dry residue is exhausted three or four times with hot fusel-oil, and the extracts are filtered through paper moistened with fusel-oil. The filtrate contains, besides strychnine, fat and colouring matter, which are got rid of by shaking the filtrate with 10 or 12 times its volume of hot water containing hydrochloric acid, the greater part of these bodies then remaining in solution in the fusel-oil, whilst the strychnine is taken up by the acidulated water. The hot acid liquid is shaken with fresh portions of fusel-oil, so long as it gives up colouring matter, and is then evaporated, mixed with a slight excess of ammonia, and again shaken with fusel-oil, which now takes up the free strychnine, and leaves it behind on evaporation. If necessary, the residue is purified by again dissolving it in hydrochloric acid, shaking with fusel-oil, &c.; it may then be recognised by the reactions given below (v. Uslar & J. Erdmann, *Ann. Pharm.* 120, 121; *J. pr. Chem.* 86, 59; *Pharm. Viertelj.* 11, 255; *Kopp's Jahresber.* 1861, 866; J. Erdmann, *Ann. Pharm.* 122, 360; *Anal. Zeitschr.* 1, 400; *Kopp's Jahresber.* 1862, 613). For other methods, some of which differ from the above only in chloroform or ether being employed instead of fusel-oil, see the following memoirs. These methods are applicable for the detection of other poisonous alkaloïds.

STAS.   *Bull. de l'Académie de Méd. de Belgique*, 9, 304; *N. J. Pharm.* 22, 281; *J. pr. Chem.* 55, 232; *Jahrb. pr. Pharm.* 24, 313; *Kopp's Jahresber.* 1851, 640.

FLANDIN.   *Compt. rend.* 86, 517; *J. pr. Chem.* 59, 185; *Chem. Gaz.* 1853, 215; *Kopp's Jahresber.* 1853, 687.

OTTO.   *Ann. Pharm.* 100, 39; abstr. *J. pr. Chem.* 70, 117; *Kopp's Jahresber.* 1856, 755.

STEVENSON MACADAM.   *Pharm. Trans.* 16, 120, and 160; *Kopp's Jahresber.* 1856, 759.

DE VRIJ & VAN DER BURG.   *Pharm. Journ.* 16, 448; *Pharm. Viertelj.* 6, 543; *N. J. Pharm.* 31, 542; *Kopp's Jahresber.* 1857, 602.

E. PROLLIUS. *N. Br. Arch.* 89, 168 ; *Chem. Centr.* 1857, 231 ; *Kopp's Jahresber.* 1857, 604.

H. SCHRÖDER. *N. Br. Arch.* 93, 190 ; *Kopp's Jahresber.* 1857, 604.

JORDAN. *N. Repert.* 10, 156 ; *Anal. Zeitschr.* 1, 131 ; *Kopp's Jahresber.* 1861, 870.

To detect strychnine in beer, Graham & Hofmann (*Pharm. Journ.* 11, 504 ; *Ann. Pharm.* 83, 39) shake the beer with animal charcoal in the proportion of 4 four ounces of charcoal to a gallon, let it stand over night, collect and wash the charcoal once or twice with cold water, and boil it for half an hour with 8 ounces of alcohol, which takes up the strychnine. The residue which remains on evaporating the alcohol, is shaken with a few drops of caustic potash and ether, the latter of which takes up strychnine, recognisable, after evaporating the solution, by means of oil of vitriol and chromate of potash.

On the means of distinguishing morphine from strychnine, see Hünefeld (*Schw.* 60, 454) ; santonine from strychnine, Wittstein (*Pharm. Viertelj.* 6, 273) : on the volumetric estimation of strychnine by means of iodomercurate of potassium, see F. F. Mayer (*Pharm. Viertelj.* 13, 43 ; *N. J. Pharm.* 46, 124 ; *Kopp's Jahresber.* 1863, 703) ; by means of biniodide of potassium, Wagner (*Dingl.* 151, 40 ; *Anal. Zeitschr.* 1, 102 ; *Kopp's Jahresber.* 1861, 867).

*Properties.* Small, white, four-sided prisms, terminated by low, four-sided pyramids (Pelletier & Caventou). Crystals of the right prismatic (rhombic) system, with the faces $y$, $i$, and $u$ (Fig. 53). Angle $y : y = 91°\ 12'$ and $88°\ 48'$ ; $i : i = 93°\ 4'$ and $86°\ 56'$ ; $u : u = 94°\ 16'$ and $85°\ 44'$. Besides these there are faces of the octahedron, the edges of which are truncated by the faces $y$, $i$, and $u$. Cleavable parallel to $y$. Lustre vitreous, pearly on the cleavage-faces. Hardness between 2 and $2\frac{1}{2}$ (Kengott, *Pogg.* 95, 614). Schabus (*Krystallgestalten,* 79) observed the faces $y$, $i$, and $u$. Angle $y : y = 90°\ 50'\ 75''$, and $89°\ 9'\ 25''$ ; $y : u = 118°\ 28'\ 5''$ ; $i : i = 93°\ 30'$ (calc. $= 93°\ 35'$) ; $u : u = 94°\ 28'$. Strychnine contaminated with a trace of lime crystallises in long, silky, flexible needles (Robiquet, *J. Pharm.* 17, 101). Strychnine is permanent in the air, and unaltered by light. It rotates a ray of polarised light to the left : in alcoholic solution $[\alpha]r = 132 \cdot 08°$ to $136 \cdot 78°$. The rotation is much less in acid solutions, but the addition of ammonia seems to restore it to the original amount (Bouchardat, *N. Ann. Chim. Phys.* 9, 213).—Strychnine does not lose weight when heated (Liebig), and does not melt without decomposition (Pelletier & Caventou ; Fresenius). According to Robiquet, Merck, and Wittstein, it is fusible without decomposition. It is inodorous, but has an intolerably bitter, afterwards somewhat metallic taste. It is the most poisonous of the vegetable bases, $\frac{1}{6}$th of a grain being sufficient to kill a large dog, with tetanic convulsions. It turns reddened litmus blue (Pelletier & Caventou). Resists putrefaction (Robin, *Compt. rend.* 32, 773).

When very small portions of powdered strychnine are carefully heated on a piece of platinum-foil having a hemispherical depression covered with a slip of glass, the glass receives an opaque white deposit of sublimed strychnine, appearing under a magnifying power of 80 diameters, to consist of round, sharply defined granules. On the addition of a drop of water, the sublimate crystallises in four-sided prisms, arranged in crosses and stars. On adding ammonia-water, it deliquesces to oil-drops, in which isolated quadratic octahedrons with truncated

summits, and groups of short, broad, four-sided prisms are formed. Addition of hydrochloric acid also causes crystallisation, partly in crossed tufts of needles, partly in broad, four-sided prisms. Very dilute chromic acid does not alter the granular deposit at first, but soon produces fine yellow crystalline stars, and ultimately double pyramids, very different from those formed with brucine under similar conditions (Helwig, *Anal. Zeitschr.* 3, 46).

|  |  |  |  |  |  | Pelletier and Dumas. |  | Liebig. *mean.* |
|---|---|---|---|---|---|---|---|---|
| 42 C | 252 | ........ | 75·44 | ........ | 77·24 | ........ | 75·35 |
| 2 N | 28 | ........ | 8·38 | ........ | 8·92 | ........ | 5·81 |
| 22 H | 22 | ........ | 6·58 | ........ | 6·54 | ........ | 6·70 |
| 4 O | 32 | ........ | 9·60 | ........ | 7·30 | ........ | 12·14 |
| C$^{42}$N$^2$H$^{22}$O$^4$ | 334 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

|  | Regnault. *mean.* |  | Gerhardt. |  | Nicholson and Abel. *mean.* |
|---|---|---|---|---|---|
| C | 74·76 | ........ | 75·66 | ........ | 75·38 |
| N | 8·45 | ........ | 8·05 | ........ | 8·66 |
| H | 6·81 | ........ | 6·90 | ........ | 6·71 |
| O | 9·98 | ........ | 9·39 | ........ | 9·25 |
|  | 100·00 | ........ | 100·00 | ........ | 100·00 |

Earlier formulæ : C$^{30}$N H$^{16}$O$^3$ and C$^{44}$N$^2$H$^{23}$O$^5$ (Liebig) ; C$^{43}$N$^2$H$^{23}$O$^4$ (Regnault) ; C$^{40}$N$^2$H$^{22}$O$^4$ and C$^{44}$N$^2$H$^{24}$O$^4$ (Gerhardt). The above formula, proposed by Regnault (*Ann. Pharm.* 29, 58), was shown by Nicholson and Abel to be correct.

*Decompositions.* 1. Strychnine, when cautiously heated, gives off colourless vapours, probably of undecomposed strychnine, and afterwards melts to a brownish liquid, which gives off a large quantity of brown vapours and leaves a carbonaceous residue (Duflos). It carbonises at 312° to 315°, and when submitted to dry distillation, puffs up, turns black, evolves carbonic acid and combustible gas, and yields an empyreumatic oil, a little water, and acetic acid, leaving charcoal (Pelletier & Caventou). — 2. Melts on platinum-foil like wax, and *takes fire* when more strongly heated, leaving a bulky charcoal (Merck). — 3. When subjected to *electrolysis*, it behaves like morphine (xvi, 425) (Hlasiwetz & Rochleder). — 4. When heated with *sulphur* to the melting-point of that body, it is decomposed, with formation of a large quantity of sulphuretted hydrogen (Pelletier & Caventou). — 5. Strychnine assumes a yellow colour with *iodine*, or in the vapour of iodine (Donné), and forms with it a peculiar compound (*q. v.*).

6. *Bromine* produces a resinous precipitate in strong solutions of hydrochlorate of strychnine; the solution contains *bromostrychnine*, which is thrown down by ammonia as a white precipitate, crystallising from alcohol in needles, and forming with hydrochloric acid a salt having a silky lustre. It contains 1 atom of bromine to 1 atom of strychnine (Laurent, *N. Ann. Chim. Phys.* 24, 312 ; *Ann. Pharm.* 69, 14). Bromine-water produces in aqueous solutions of strychnine a white turbidity, which disappears on agitation; the liquid, which is yellow at first, becomes colourless in 24 hours. Dilute solutions of

strychnine salts (containing $\frac{1}{300}$th to $\frac{1}{500}$th of strychnine) give a curdy yellowish-white precipitate with bromine-water (Duflos ; Merck).

7. Dry *chlorine* does not act upon strychnine or its salts (Marchand), but when the gas is passed into water in which strychnine is suspended, an evolution of heat takes place, and chorostrychnine is formed as a white scum ; hydrochlorate of strychnine is also produced at first, but by the further action of chlorine it is entirely converted into chorostrychnine, so that the nearly colourless liquid contains in solution only hydrochloric acid, with the exception of a few flocks precipitable by ammonia. Salts of strychnine immediately yield the white scum with chlorine (Pelletier). A turbidity and precipitate are produced even in a solution of 1 part of acetate of strychnine in 5,000 or 8,000 parts of water (Marchand, *J. pr. Chem.* 14, 191). The precipitate is formed gradually, and only in presence of excess of chlorine (De Vrij & Van der Burg). The turbidity produced by chlorine-water in water containing $\frac{1}{500}$th of acetate of strychnine is increased by heat (Merck). An aqueous solution of strychnine is not affected by chlorine-water (Duflos). The precipitate is not coloured by nitric or sulphuric acid (Lepage, *J. Pharm.* 26, 140 ; *N. Br. Arch.* 25, 300) ; it forms a colourless solution in ammonia (Fresenius), and dissolves easily in ether and alcohol (Pelletier ; Riegel, *N. Br. Arch.* 58, 274). — Chlorine passed into a hot aqueous solution of hydrochlorate of strychnine forms Laurent's chlorostrychnine (p. 515).

*Solution of chloride of lime* throws down from dilute solutions of acetate of strychnine, a white precipitate insoluble in dilute sulphuric and acetic acids, but easily soluble in alcohol, also in glacial acetic acid and alkaline liquids (Horsley).

8. Aqueous hydrochlorate of strychnine boiled with *nitrite of potassium* evolves nitrogen and forms oxystrychnine and bioxystrychnine (Schützenberger). By taking up 6 atoms of water and 2 or 4 atoms of oxygen. — 9. Strychnine dissolves very rapidly in *fuming nitric acid*, forming a greenish-yellow solution, which turns lemon-yellow when diluted with water (Duflos). Nitric acid of sp. gr. 1·2 forms a white salt (Duflos). Even the strong acid does not colour strychnine in the cold (Robiquet), but when heated, turns it brownish-yellow, without evolving red vapours : after cooling, water throws down from the non-unctuous mass a yellow precipitate which melts in boiling water to a yellow resin, afterwards dissolves, and is deposited from the solution on cooling in yellow shining crystalline nodules. The precipitate dissolves very easily in alcohol, and explodes when heated (Gerhardt, *Compt. chim.* 1845, 136). This body is probably nitrate of nitrostrychnine, and the same product which Pelletier & Caventou regarded as acid nitrate of strychnine (Nicholson & Abel). To this place belong also the orange-coloured tufts of needles which Ménétriès obtained by warming strychnine with strong nitric acid and evaporating the solution rapidly ; they explode when heated, evolving nitric oxide. The further action of nitric acid produces oxalic acid (Pelletier & Caventou). On treating the products formed by nitric acid with caustic potash, volatile bases are set free (Anderson). Strychnine containing brucine (Robiquet), and consequently commercial strychnine (Lefort), turns red with nitric acid.

10. Cold *oil of vitriol* does not colour strychnine : *fuming sulphuric acid* colours it slightly brown, and when heated with it forms a greenish-yellow solution (Duflos). *Oxidising agents* produce with solutions of sulphate of strychnine containing a large excess of sulphuric acid, characteristic colours, which serve for the detection of very small quantities of strychnine (Marchand ; Lefort).

*a.* When the solution in oil of vitriol is made in a platinum basin, and the platinum is connected with the positive pole, and a platinum wire dipping into the acid with the negative pole of one cell of a galvanic battery, a purple-red coloration is produced (Letheby, *Pharm. Journ.* 16, 10 ; *Kopp's Jahresber.* 1856, 758).

*b.* On dissolving strychnine in oil of vitriol containing 1 p. c. of nitric acid, and adding a trace of *peroxide of lead,* a blue coloration is produced, passing to violet, red, and in a few hours to yellow (E. Marchand, *J. Chim. méd.* 20, 15). Or the strychnine may be triturated with peroxide of lead and the oil of vitriol containing nitric acid dropped upon the mixture (E. Marchand, *N. J. Pharm.* 4, 200). The violet colour appears also in the absence of nitric acid, and is then more permanent, but it is produced only with concentrated sulphuric acid, since water destroys it (Lefort, *Rev. scient.* 16, 355; also *N. J. Pharm.* 21, 172). Marchand (*J. Chim. méd.* 24, 197 ; *J. pr. Chem.* 44, 185), on the contrary, considers the addition of nitric acid advantageous. Riegel (*Jahrb. pr. Pharm.* 8, 290) and Wittstein employ sulphuric acid of sp. gr. 1·4. Solutions of strychnine-salts give the blue colour only after evaporation to dryness (Riegel).

*c.* On adding *bichromate of potash* to a solution of strychnine in oil of vitriol spread out upon porcelain, violet streaks make their appearance in the liquid, starting from the bichromate, after which the whole liquid acquires a fine violet colour, or with a larger quantity of strychnine a pure blue (Otto, *J. pr. Chem.* 38, 511; also *Ann. Pharm.* 100, 50 ; L. Thomson, *Pharm. Journ.* 9, 24 ; *N. J. Pharm.* 17, 276 ; *Lieb. Kopp's Jahresber.* 1850, 617). It is better to employ the bichromate in lumps than in powder or solution (Otto).

*d.* *Ferrocyanide of potassium* produces with strychnine a dark-violet coloration, more permanent than that produced with bichromate of potash : the colour may be obtained also in presence of other organic substances (Davy, *N. J. Pharm.* 24, 204). This colour also passes through red into yellow, though more slowly than that obtained in *c* *Ann. Pharm* 88, 402). Nitroprusside of sodium proposed by Horsley (*Chem. News,* 1862, 341) as a reagent, acts only when it contains ferrocyanide of potassium (Rodgers ; Neubauer; Werther).

*e.* On adding small portions of *black oxide of manganese* to a solution of strychnine in pure oil of vitriol, or in sulphuric acid containing nitric acid (prepared according to xvi, 141), a violet-purple coloration is immediately produced, passing into dark-red in the course of an hour. The colour remains unchanged when the liquid is slowly diluted with four to six times its volume of water, and on nearly neutralising the solution with ammonia, the violet-purple colour reappears. When supersaturated with ammonia, the liquid becomes yellowish-green to yellow, but on acidifying it with dilute sulphuric acid, the violet-purple colour again makes its appearance (J. Erdmann, *Ann. Pharm.* 120, 188). Mack had previously employed manganese and sulphuric acid for the recognition of strychnine (*N. Br. Arch.* 46, 314).

*f.* *Chloric acid* and *chlorates, chlorous acid, iodic acid* and *iodates,*

also *sulphate of manganese* and *permanganate of potash* produce in the sulphuric acid solution of strychnine, similar colorations, or a red colour which in some cases quickly disappears (Lefort). The violet colour produced by iodic acid passes gradually into red-brown, which colour remains permanent for many days (Landerer, *Pharm. Zeitschr.* 1, 86). Concerning this reaction, see also Copney (*Pharm. J. Trans.* 16, 23 ; *Pharm. Vierteljr.* 6, 80 : Guy, *Pharm. J. Trans.* [2], 2, 558 and 602 ; 3, 11 and 12 ; *Anal. Zeitschr.* 1, 90 and 92) : De Vrij and Van der Burg (*loc. cit.*).

Strychnine dissolved in a large quantity of milk may also be detected by means of peroxide of lead and oil of vitriol containing nitric acid (Erdmann & Marchand, *J. pr. Chem.* 31, 374). The presence of santonin or starch does not prevent the recognition of strychnine by bichromate of potash and oil of vitriol: sugar, quinine, or morphine renders this reaction indistinct, but not that with peroxide of manganese (Brieger, *Jahrb. pr. Pharm.* 20, 87). Strychnine may be detected by chromate of potash even in presence of quinine, cinchonine, starch, or dextrin, provided the oil of vitriol be added first (Vogel, *N. Repert. Pharm.* 2, 560). The presence of morphine is prejudicial to the strychnine-reactions (Reese, *Chem. News,* 1862, 316 ; *Chem. Centr.* 1862, 557 : Horsley). Thomas (*Amer. Journ. Pharm.* 1862, 227), on the contrary, finds that strychnine is recognisable even when mixed with 3 parts of morphine. The two bases may be separated by means of caustic potash, which does not dissolve strychnine ; or by chloroform, which dissolves only strychnine (Thomas, *Chem. News,* 5, 352) ; or by benzene, which dissolves strychnine very easily, but not morphine (Rodgers, *Chem. News,* 6, 15) ; neutral chromate of potash also throws down from a strong solution of the two bases, after brisk stirring, a golden-yellow crystalline precipitate of chromate of strychnine, whilst the morphine-salt crystallises only after a longer time (Horsley). Ferrocyanide of potassium may be advantageously substituted for the neutral chromate (Neubauer).

Tartar-emetic, tartaric acid, and bitartrate of potash prevent the detection of strychnine by chromate of potash and oil of vitriol when the alkaloïd is present in the form of nitrate, but not when pure. Strychnine as nitrate may be detected by peroxide of lead and oil of vitriol, even in presence of tartrates (Gorup-Besanez, *Handwörterb.* [2] 1, 468 ; *Kopp's Jahresber.* 1856, 757). Pure strychnine, or the hydrochlorate or acetate, may be distinctly recognised by means of chromate of potash and sulphuric acid when mixed with 20 or 30 parts, but not distinctly when mixed with 60 parts of tartar-emetic. The presence of a large quantity of sugar or tartaric acid does not interfere with the reaction in the case of hydrochlorate and acetate of strychnine, but a mixture of 1 part of nitrate of strychnine with 20 parts or more of tartar-emetic immediately assumes a green colour. The strychnine reaction is obtained, however, with peroxide of lead and oil of vitriol, even when a mixture of 1 part of nitrate of strychnine and 60 parts of tartar-emetic is employed (Hagen, *Ann. Pharm.* 103, 159). — According to Bingley (*Chem. Gaz.* 1856, 229 ; *Kopp's Jahresber.* 1856, 757), terchloride of antimony interferes with the bichromate of potash reaction.

*Dilute sulphuric acid,* added to a mixture of *chlorate of potash* and strychnine, produces Rousseau's strychnic acid, or when the action proceeds further, a red resinous colouring matter, soluble in water and alcohol, but insoluble in ether (Rousseau).

To prepare strychnic acid, Rousseau triturates 3 parts of strychnine with 1 part of chlorate of potash and a little water, and drops oil of vitriol upon the mixture, whereupon it becomes hot and acquires a transient red colour; after which he dilutes and boils. If the reaction is incomplete, pure strychnine (!), or the sulphate crystallises from the liquid as it cools, and on evaporating the mother-liquor colourless acid needles of strychnic acid are deposited. The crystals do not taste bitter; they decompose when heated, leaving charcoal, and are soluble in water and slightly in alcohol, and form crystallisable salts with potash and oxide of copper (Rousseau, *J. Chim. méd.* 20, 415).

When strychnine is treated with *peroxide of lead* and *dilute sulphuric acid* (in the same manner as cinchonine, p. 202), a straw-yellow powder is obtained, which dissolves very slightly in cold, and somewhat more freely in boiling water, and is deposited from a solution in hot water containing sulphuric acid on cooling. It dissolves in alcohol, and very easily in caustic potash, which it seems to neutralise (C. Marchand, *N. J. Pharm.* 4, 28; *J. Chim. méd.* 20, 366).

11. Hot solutions of *iodic acid* colour strychnine and its salts violet-red, and produce a black precipitate on standing (Riegel). — 12. *Chromic acid* colours it violet-blue (Eboli).

13. Strychnine cautiously heated with lumps of solid hydrate of potash, forms a red-brown mass, from a solution of which in boiling water, acids evolve a disagreeable odour, and throw down an abundance of yellow flocks, which are deposited from their solution in boiling alcohol on cooling, and are insoluble in water, ether, and cold alcohol. — On melting strychnine with hydrate of potash, the mass turns brown and black, evolves hydrogen with slight intumescence, gives off water and a little chinoline (xiii, 244), whilst carbonate of potash remains in the residue (Gerhardt).

14. *Iodide of methyl* (Stahlschmidt), *iodide of ethyl, chloride of amyl* (How), *bibromide of ethylene* (Ménétriès), form derivative compounds (pp. 506-514).

15. With *chloride of benzoyl*, strychnine forms hydrochlorate of strychnine and *benzostrychnide*, $C^{42}N^2H^{21}(C^{14}H^5O^2)O^4$, a white bitter product, which melts above 100°, solidifies in a crystalline mass, and is very slightly soluble in water and insoluble in acids, but easily soluble in alcohol and ether (Schützenberger).

16. Strychnine is not decomposed in contact with a fermenting mixture of sugar and *yeast* (Larocque & Thibierge, *J. Chim. méd.* 18, 689). — 17. It is not decomposed in the animal organism, nor by *putrefaction* after death; it has been detected three years after death in the bodies of animals poisoned with it (Macadam, *loc. cit.*: Rodgers & Girdwood, *Pharm. Journ.* 16, 497; *Pharm. Viertelj.* 6, 549; *Kopp's Jahresber.* 1857, 603). See also J. Erdmann (*Ann. Pharm.* 122, 360); De Vrij & Van der Burg (*loc. cit.*).

*Combinations.* — A. *With Water.* — Strychnine dissolves in 6,667 parts of cold, and in 2,500 parts of boiling water (Pelletier & Caventou). According to Duflos, it dissolves in about 6,000; according to Abl, in 7,200 parts of water. The cold solution diluted with 100 times its bulk of water, still tastes distinctly bitter (Pelletier & Caventou).

Strychnine does not dissolve in aqueous *ammonia* (Merck); neither does *caustic potash* increase its solubility in water (Duflos).

B. *With Iodine.*—Tincture of iodine or biniodide of potassium produces in solutions of strychnine-salts, a dense kermes-brown precipitate; a cold aqueous solution of strychnine, however, is not affected by iodine-water (Duflos). A solution of 1 part of strychnine in 1 part of alcohol and 3 parts of water, when warmed with a little tincture of iodine and left to cool spontaneously, deposits crystals of an iodine-compound, probably $C^{42}N^2H^{22}O^4,I^2$. The crystals are six-sided prisms, exhibiting in a very high degree the property of double absorption of light (Herapath, *Chem. Gaz.* 1855, 320; 1856, 394; *Kopp's Jahresber.* 1855, 568; 1856, 758). On precipitating with tincture of iodine, a solution of strychnine in weak alcohol acidified with hydrochloric or hydriodic acid, and dissolving the brown precipitate in boiling alcohol, highly lustrous red-brown prisms are obtained, which do not lose weight at 140°, and are represented by the formula $C^{42}N^2H^{22}O^4,HI,2I$ (Tilden, *Chem. Soc. J.* [2] 3, 99).

When 2 parts of strychnine are triturated with 1 part of iodine, a brown mass is obtained, which gives up to cold water traces only, and to boiling water a small quantity of hydriodate of strychnine. Boiling alcohol dissolves the mass, and when cooled and concentrated, deposits laminæ of iodostrychnine of the colour of mosaic gold, and afterwards crystals of hydriodate of strychnine. — The laminæ are nearly tasteless at first, but afterwards taste bitter and harsh; they evolve iodine when heated, and carbonise without melting. They are decomposed by oil of vitriol and by strong nitric acid, with separation of iodine, and by hydrochloric acid when heated therewith. They set free strychnine when heated with caustic potash (not with ammonia), and are decomposed by nitrate of silver, even in the cold, iodide of silver and nitrate of strychnine being formed. They are easily soluble in boiling alcohol, very slightly soluble in boiling water, and insoluble in ether (Pelletier).

| | | | | Pelletier. | | Regnault. |
|---|---|---|---|---|---|---|
| 84 C | 504 | ........ | 48·04 | ........ | 49·53 | ........ 47·75 |
| 4 N | 56 | ........ | 5·34 | | | |
| 44 H | 44 | ........ | 4·19 | ........ | ........ | 4·54 |
| 8 O | 64 | ........ | 6·10 | | | |
| 3 I | 381 | ........ | 36·33 | ........ | 39·50 | |
| 2 $C^{42}N^2H^{22}O^4,3I$ | 1049 | ........ | 100·00 | | | |

C. *With Acids.* — Strychnine dissolves easily in acids, even when very dilute, neutralising them completely. It also precipitates the oxides from most of the salts of the heavy metals, though often only partially, double salts being formed. — The salts of strychnine are for the most part crystallisable, extremely bitter, and on account of their solubility, more highly poisonous than pure strychnine. Alkalis and their carbonates (and magnesia) precipitate strychnine from its salts, in the form of a pulverulent precipitate, which does not dissolve to any great extent in excess of the precipitant, and crystallises after a time in delicate closely grouped needles. The precipitate thrown down by ammonia from a solution of strychnine in dilute hydrochloric acid, dissolves in excess of the precipitant, but in a short time the strychnine crystallises from the ammoniacal liquid in distinct needles

(Fresenius). See also Anderson (*N.*J. Pharm.* 13, 443). Bicarbonate of soda throws down strychnine from neutral, moderately strong solutions of its salts; on dropping an acid into the liquid, in quantity not sufficient to decompose the whole of the alkaline carbonate, the carbonic acid set free dissolves the precipitate. Bicarbonate of soda does not throw down a precipitate in acid solutions of strychnine, but crystals are formed in the liquid on standing, or a precipitate is formed on boiling (Fresenius). Very dilute solutions of strychnine, mixed with tartaric acid, are not (or at least not immediately) precipitated by alkaline bicarbonates ; less dilute solutions deposit needles in a quarter of an hour, the whole of the strychnine crystallising out (Oppermann, *Compt. rend.* 21, 810 ; *J. pr. Chem.* 36, 445). The salts of strychnine (and the alkaloïd itself) are recognised by their behaviour with chlorine-water, nitric acid, chromate of potash and oil of vitriol, sulphocyanide of potassium, and mercuric chloride. (See above.) On the delicacy of the particular reactions, see Wormley (*Sill. Amer. J.* [2] 28, 216 ; *J. pr. Chem.* 80, 382).

*Carbonate of Strychnine.* — The precipitate thrown down from strychnine-salts by alkaline carbonates is free from carbonic acid (How ; Langlois) (contrary to Pelletier & Caventou) ; but an unstable carbonate of strychnine may be obtained by decomposing hydrochlorate of strychnine with carbonate of silver (How). — Freshly precipitated strychnine dissolves easily in an aqueous solution of carbonic acid (Pelletier & Caventou); after standing some time at 0°, the solution deposits crystals, which do not evolve carbonic acid, either with acids, or at a temperature of 300° (Langlois, *N. Ann. Chim. Phys.* 48, 502 ; *Ann. Pharm.* 100, 374).

Strychnine combines with metaphosphoric acid (Nicholson & Abel).

*Phosphate of Strychnine.* — Ordinary bisodic phosphate throws down from strychnine-salts a granular crystalline precipitate (v. Planta). — A. *Bibasic.* — An aqueous solution of B is digested for some time with finely powdered strychnine, and the crystals which separate are purified by two or three crystallisations. The mother-liquor contains a large quantity of the salt B. — Large rectangular tables, often so thin as to exhibit a splendid green colour. The salt does not redden litmus. It is much less soluble in water than B. — The crystals lose 17·6 p. c. of water at 100° (18 at. = 17·45 p. c. HO) (Anderson), and are also rendered anhydrous by drying over oil of vitriol in a vacuum (Nicholson & Abel).

|  |  | at 121°. |  |  | Anderson. |
|---|---|---|---|---|---|
| 84 C | ............................................. | 504 | ........ | 65·79 | ........ 66·51 |
| 4 N | ............................................. | 56 | ........ | 7·31 | ........ |
| 47 H | ............................................. | 47 | ........ | 6·13 | ........ 6·54 |
| 11 O | ............................................. | 88 | ........ | 11·49 | |
| PO⁵ | ............................................. | 71 | ........ | 9·28 | |
| 2 (C⁴²N²H²⁰O⁴,HO),HO,PO⁵ | .... | 766 | ........ | 100·00 | |

B. *Neutral.* — Prepared by digesting strychnine with moderately strong phosphoric acid, the solution, on cooling, crystallising in radiated groups of long needles, which redden litmus and have a very bitter taste. — The salt dissolves in 5 or 6 parts of cold, and in a much smaller quantity of hot water. — At 127° [or over oil of vitriol in a vacuum

(Nicholson & Abel)] it loses 7·95 p. c. of water (4 at. = 7·69 p. c. HO) (Anderson, *Ann. Pharm.* 66, 55; *Quart. J. Chem. Soc.* 1, 55.)

| | Dried. | | Regnault. at 140° | Anderson. | | |
|---|---|---|---|---|---|---|
| 42 C | 252 | .... | 58·33 | 59·85 | .... 58·72 | .... 59·05 |
| 2 N | 28 | .... | 6·48 | | | |
| 25 H | 25 | .... | 5·78 | 5·85 | .... 5·96 | .... 5·97 |
| 7 O | 56 | .... | 12·97 | | | |
| PO⁵ | 71 | .... | 16·44 | | | |

$C^{42}N^2H^{22}O^4,HO,PO^5$ + 2aq..... 432 .... 100·00

Regnault's salt probably contained an admixture of A (Anderson).

Monosodic phosphate does not form with strychnine a double salt of phosphate of soda and phosphate of strychnine (Anderson).

*Hydrosulphate of Strychnine.* — Strychnine suspended in water is dissolved by a current of hydrosulphuric acid, forming a colourless, very bitter solution, which leaves pure strychnine when evaporated (Pelletier & Caventou).

*Hyposulphite of Strychnine.* — Formed in a mixture of strychnine, alcohol, and hydrosulphate of ammonia on standing in the air. — Large rhombic plates. Neutral. Loses 3·91 to 4·3 p. c. of water at 200° (2 at. = 4·3 p. c. HO). Dissolves in 114 parts of cold, and in a smaller quantity of hot water (H. How, *Pharm. Centr.* 1855, 95).

| | at 100° | | | | How. mean. |
|---|---|---|---|---|---|
| 42 C | 252 | ........ | 63 | ........ | 63·07 |
| 2 N | 28 | ........ | 7 | | |
| 24 H | 24 | ........ | 6 | ........ | 5·93 |
| 8 O | 64 | ........ | 16 | | |
| 2 S | 32 | ........ | 8 | ........ | 8·29 |

$C^{42}N^2H^{22}O^4,HO,S^2O^2$ + aq. .... 400 ........ 100

*Sulphate of Strychnine.* — A. *Neutral.* — Obtained by saturating dilute sulphuric acid with finely powdered strychnine (Nicholson & Abel). Small transparent cubes (Pelletier & Caventou); large four-sided prisms (Nicholson & Abel). The cubes turn dull in the air, without losing weight, and melt in their water of crystallisation at a gentle heat (Pelletier & Caventou). The salt loses 13·08 p. c. of water at 135° (7 at. = 14·1 p. c. HO) (Regnault). Neutral (Nicholson & Abel). Rotates a ray of polarised light to the left; $[\alpha]r = 25·58°$ for the salt dried at 40° (Bouchardat). — Dissolves in less than 10 parts of water (Pelletier & Caventou), in 48 parts (Abl), in about 50 parts (Bouchardat).

The anhydrous salt forms crystals belonging to the square prismatic or quadratic system. Octahedrons with basal face (*fig.* 24). Angle $p : e = 102° 3'$; $e : e' = 92° 30'$; $e : e'' = 155° 54'$. The edge formed by $p$ and $e$ is truncated by the face of a second octahedron, forming with $p$ an angle of 125° 26', and with $e$ an angle of 156° 37''. Cleavable parallel to $p$ (Descloizeaux, *Compt. rend.* 44, 909; *Pogg.* 102, 474). Rammelsberg (*Krystall. Chemie*, 380) observed the following angles: $p : e = 101° 40'$; $e : e' = 92° 20'$; $e : e'' = 156° 40'$; and between $p$ and $e$ the truncation-face of a more obtuse octahedron, forming with $p$ an angle

of about 160°. — The salt with 7 atoms of water belongs to the right prismatic or rhombic system : the simplest form as in *fig.* 65.   Angle $u : t = 107° \ 14'$; $u : u' = 145° \ 30'$; $t : i = 137° \ 48'$; $i : i$ above $84° \ 24'$ : between $u$ and $t$ there is a truncation-face, forming with $t$ an angle of $125° \ 45'$.   The angle $i : i$ is sometimes replaced by two horizontal prisms, one of which forms with $t$ an angle of $118° \ 40'$, the other an angle of $99° \ 50'$.   The parallel $u$-faces often disappear, in which case the crystals assume the form of monoclinic prisms.   The $t$-faces are prominently developed, so that the crystals have the form of square tables with bevelled edges.   The crystals have a glassy lustre; pearly on the face $t$ (Schabus, *Krystallgestalt.* 80).

|  | Dried. | | | Liebig. at 100° | | Regnault. at 130°–205° | | Nicholson & Abel. in vacuo. |
|---|---|---|---|---|---|---|---|---|
| 42 C | 252 | .... | 65·80 | .... | 64·76 | .... | 65·35 | .... 65·68 |
| 2 N | 28 | .... | 7·31 | | | | | |
| 23 H | 23 | .... | 6·01 | .... | 5·99 | .... | 6·10 | .... 6·17 |
| 5 O | 40 | .... | 10·44 | | | | | |
| SO³ | 40 | .... | 10·44 | .... | ... | | .... | 10·44 |
| C⁴²N²H²²O⁴,HO,SO³ .... | 383 | .... | 100·00 | | | | | |

B. *Acid.* — Obtained from A by the addition of sulphuric acid. Long, thin, very acid needles (Nicholson & Abel).

|  |  |  |  | Nicholson & Abel. |
|---|---|---|---|---|
| 42 C | 252 | ........ | 58·33 | ........ 58·73 |
| 2 N | 28 | ........ | 6·48 | |
| 24 H | 24 | ........ | 5·56 | ........ 5·83 |
| 6 O | 48 | ........ | 11·12 | |
| 2 SO³ | 80 | ........ | 18·51 | ........ 18·33 |
| C⁴²N²H²²O⁴,2(HO,SO³) .... | 432 | ........ | 100·00 | |

*Sulphate of Iodostrychnine.* — When the brown-red precipitate thrown down by biniodide of potassium in solutions of strychnine, is dissolved in alcohol containing sulphuric acid, the solution yields crystals of sulphate of iodostrychnine, which polarise light (De Vrij and Van der Burg).   Stellate groups of prisms, of a fine green colour by reflected, deep blood-red by transmitted light, thick crystals being quite opaque (Herapath).

*Iodate of Strychnine.* — Iodic acid produces neither colour nor precipitate in aqueous solutions of strychnine (v. Planta).   See above.   On gently heating strychnine in aqueous iodic acid, the solution, in the absence of brucine, assumes a wine-red colour, and yields when concentrated, long tufts of needles, which are coloured red on the surface, and may be decolorised by washing with cold water.   The crystals dissolve very easily in water (Serullas, *Ann. Chim. Phys.* 45, 275; *Pogg.* 20, 595).   When strychnine suspended in warm water is exactly neutralised with iodic acid, or when iodate of baryta is decomposed by sulphate of strychnine, long flat pearly needles are obtained, containing 45·92 p. c. of carbon and 42·80 of iodic acid (Pelletier).

*Periodate of Strychnine.* — On dissolving strychnine in warm aqueous periodic acid, colourless, highly lustrous, rectangular prisms [6-sided prisms, terminated by 4-sided pyramids (Langlois)] are obtained, which effloresce over oil of vitriol, explode violently when heated, and

dissolve with moderate facility in hot water and alcohol. The aqueous solution turns brown when evaporated in the air (Bödeker, *Ann. Pharm.* 71, 64; Langlois, *N. Ann. Chim. Phys.* 34, 278; *Ann. Pharm.* 83, 174).

*Hydriodate of Strychnine.* — Iodide of potassium throws down from strychnine-salts a dense crystalline precipitate (v. Planta). On washing the precipitate with water, dissolving it in alcohol, and evaporating the solution, glassy four-sided needles are obtained (Merck). The salt may also be prepared by dissolving strychnine in aqueous hydriodic acid (Pelletier), but the excess of acid must be quickly removed by washing, as otherwise decomposition-products are formed (Nicholson & Abel). Small white laminæ or needles, which do not lose weight in a vacuum. Neutral and very bitter. Dissolves slightly in cold water and much more freely in alcohol (Pelletier).

|  | Crystals. |  |  |  | Pelletier. |  | Nicholson & Abel. mean. |
|---|---|---|---|---|---|---|---|
| 42 C | 252 | ........ | 54·62 | ........ | 55·08 | ........ | 54·60 |
| 2 N | 28 | ........ | 6·07 |  |  |  |  |
| 23 H | 23 | ........ | 4·98 | ........ |  | ........ | 5·02 |
| 4 O | 32 | ........ | 6·95 |  |  |  |  |
| I | 127 | ........ | 27·38 | ........ | 26·12 | ........ | 27·12 |
| $C^{42}N^2H^{22}O^4,HI$ .... | 462 | ........ | 100·00 |  |  |  |  |

*Hydrobromate of Strychnine.* — Formed by dissolving strychnine in aqueous hydrobromic acid, and leaving the solution to crystallise (Nicholson & Abel).

|  | In a vacuum. |  |  |  | Nicholson & Abel. |
|---|---|---|---|---|---|
| 42 C | 252 | ........ | 60·72 | ........ | 60·83 |
| 2 N | 28 | ........ | 6·74 |  |  |
| 23 H | 23 | ........ | 5·54 | ........ | 5·60 |
| 4 O | 32 | ........ | 7·71 |  |  |
| Br | 80 | ........ | 19·29 | ........ | 18·69 |
| $C^{42}N^2H^{22}O^4,HBr$ .... | 415 | ........ | 100·00 |  |  |

*Chlorate of Strychnine.* — The rose-red solution of strychnine in aqueous chloric acid deposits thin short prisms, or solidifies completely when concentrated. — Iodic acid throws down from a solution of the salt a precipitate of iodate of strychnine (Serullas, *Ann. Chim. Phys.* 45, 280).

*Perchlorate of Strychnine.* — Obtained from perchlorate of baryta and sulphate of strychnine. — Small colourless or pale-yellow, glassy rhombic prisms, which after drying at 30° become opaque at 170°, losing 3·8 p. c. of water, and explode when more strongly heated. — Dissolves slightly in cold water, and much more freely in alcohol (Bödeker, *Ann. Pharm.* 71, 62).

|  | Crystals. |  |  |  | Bödeker. |
|---|---|---|---|---|---|
| $C^{42}N^2H^{22}O^4,HO$ | 343 | ........ | 75·80 | ........ | 76·99 |
| $ClO^7$ | 91·5 | ........ | 20·22 | ........ | 19·21 |
| 2 HO | 18 | ........ | 3·98 | ........ | 3·80 |
| $C^{42}N^2H^{22}O^4,HO,ClO^7 + 2aq.$ .... | 452·5 | ........ | 100·00 | ........ | 100·00 |

*Hydrochlorate of Strychnine.* — 100 parts of strychnine take up 14·6 to 15·02 of hydrochloric acid gas (Liebig). When exposed to a current

of hydrochloric acid gas, and afterwards heated to 150, 100 parts of strychnine retain 10·67 parts of hydrochloric acid (Regnault) (1 at. = 10·93 parts HCl.). — A solution of strychnine in warm aqueous hydrochloric acid solidifies to a silky mass of needles (Regnault). The salt is neutral towards vegetable colours (Nicholson & Abel). It exerts a left-handed rotatory action on polarised light; $[\alpha]r = 28·18°$. Dissolves in about 50 parts of water at 22° (Bouchardat). — The needles lose the whole of their water of crystallisation, amounting to 7·17 p. c., at 120°, or in a vacuum (3 at. = 6·79 p. c. HO) (Nicholson & Abel). According to Gerhardt, on the contrary, the salt dried at 100° loses 4·81 p. c. (= 2 at.) of water, at 130° only.

| | Dried. | | | Regnault. at 130° | | Gerhardt. at 160° | | Nicholson. & Abel. mean. |
|---|---|---|---|---|---|---|---|---|
| 42 C | 252 | .... | 68·01 | .... | 68·01 | .... | 65·08 | .... | 67·82 |
| 2 N | 28 | .... | 7·56 | .... | 7·40 | | | | |
| 23 H | 23 | .... | 6·20 | .... | 6·77 | .... | 6·94 | .... | 6·43 |
| 4 O | 32 | .... | 8·65 | | | | | | |
| Cl | 35·5 | .... | 9·58 | .... | 9·33 | .... | | | 9·55 |

C⁴²N²H²²O⁴,HCl .... 370·5 .... 100·00

*Hydrofluate of Strychnine.* — Strychnine dissolves in hydrofluosilicic acid, with separation of silica. — The easily formed solution of strychnine in warm aqueous hydrofluoric acid yields crystals, which give off hydrofluoric acid over hydrate of lime. — Colourless right rhombic prisms, having an acid reaction, slightly soluble in cold, easily in hot water, and sparingly soluble in alcohol. — The salt loses 5·9 p. c. of water (3 at. = 6 p. c. HO) over oil of vitriol, becoming opaque, soft, and sticky. At 100° it gives off 7·43 p. c. of water (4 at. = 8 p. c.), and not more at 150°; at a higher temperature it reddens and is decomposed (Elderhorst, *Ann. Pharm.* 74, 77).

| | Over oil of vitriol. | | | | Elderhorst. mean. |
|---|---|---|---|---|---|
| 42 C | 252 | ........ | 59·61 | ......: | 59·33 |
| 2 N | 28 | ........ | 6·61 | | |
| 27 H | 27 | ........ | 6·33 | ........ | 6·15 |
| 5 O | 40 | ........ | 9·50 | | |
| 4 F | 75·2 | ........ | 17·95 | | |

C⁴²N²H²²O⁴,4HF + aq. .... 422·2 ........ 100·00

Elderhorst likewise found the per-centage of strychnine in the salt, and the increase in weight on evaporating strychnine with excess of hydrofluoric acid, to agree with the above formula.

*Nitrate of Strychnine.* —When strychnine is dissolved in nitric acid diluted till it tastes faintly acid, fine colourless needles of the nitrate are obtained on cooling. Strong nitric acid forms decomposition-products, but no acid salt (Nicholson and Abel). — Silky tufts of long, flexible needles, very bitter, and even more poisonous than pure strychnine. Neutral. When heated to a little over 100°, it turns yellow, swells up, and decomposes violently, without development of light (Pelletier & Caventou). Rotates a ray of polarised light to the left; for the salt dried at 40°, $[\alpha]r = 29·25°$ (Bouchardat). — Soluble in 50 parts of cold water (Cap & Garot); in 80 parts of water at 18·75° (Abl); in 2 parts of boiling water (Wittstein). Soluble in 60 parts of

cold, and 2 parts of boiling alcohol of 80 p. c. (Wittstein); in 26 parts of glycerin, and in 400 parts of fat oil (Cap & Garot). Insoluble in ether (Pelletier & Caventou).

|  |  |  |  |  | Regnault. at 130° mean. |  | Ettling & Will. |  | Nicholson & Abel |
|---|---|---|---|---|---|---|---|---|---|
| 42 C | .............................. | 252 | .... | 63·47 | .... | 63·24 | .... | 63·55 | .... | 63·40 |
| 3 N | .............................. | 42 | .... | 10·58 | .... | 10·35 |  |  |  |
| 23 H | .............................. | 23 | .... | 5·79 | .... | 5·89 | .... |  | .... | 5·85 |
| 10 O | .............................. | 80 | .... | 20·16 | .... | 20·52 |  |  |  |
| $C^{42}N^2H^{22}O^4,HO,NO^5$ | .... | 397 | .... | 100·00 | .... | 100·00 |  |  |  |

*Phosphantimonic acid* (xiv, 227) produces in solutions of strychnine-salts a copious, yellowish-white curdy precipitate, or in more dilute solutions a cloudiness only (Schultze). — *Phosphomolybdic acid* (xiii, 164) precipitates strychnine yellowish-white (Sonnenschein); *metatungstic acid* precipitates it from more dilute solutions (Scheibler, *J. pr. Chem.* 80, 204).

*Chromate of Strychnine.* — A. *Neutral.* — Neutral chromate of potash throws down from solutions of strychnine-salts an amorphous precipitate (Horsley), consisting, according to André, of a mixture of acid salt with free strychnine. — The yellowish-brown precipitate, separated from the mother-liquor and dissolved in hot water, deposits on cooling, orange-yellow needles, which are neutral and sparingly soluble in water and alcohol (Nicholson & Abel).

|  |  |  | at 100°. |  |  | Nicholson and Abel. |
|---|---|---|---|---|---|---|
| $C^{42}N^2H^{22}O^4$ | ........................... | 334 | ........ | 84·53 |  |  |
| $HO,CrO^3$ | ......................... | 61·2 | ........ | 15·47 | ........ | 15·34 |
| $C^{42}N^2H^{22}O^4,HO,CrO^3$ | ........ | 395·2 | ........ | 100·00 |  |  |

B. *Acid.* — Acetate of strychnine is completely precipitated by free chromic acid, and also by a mixture of 1 part of bichromate of potash with 14 volumes of water and 2 volumes of oil of vitriol, dilute solutions of chromic acid, producing groups of small crystals and cubes, and stronger solutions at once throwing down, even from very weak solutions of strychnine, a gold-coloured precipitate, which turns darker on exposure to light (Horsley, *Pharm. J. Trans.* 16, 177; *J. pr. Chem.* 72, 312; *Inst.* 1856, 463; *Kopp's Jahresber.* 1856, 758). Long, orange-red needles, but little soluble in water (André, *N. J. Pharm.* 41, 341). Assumes a purple-red colour in oil of vitriol (De Vrij & Van der Burg).

*Arsenite of Strychnine.* — $C^{42}N^2H^{22}O^4,HO,AsO^3$. Formed by heating 12·38 parts of arsenious acid with 800 parts of water and 10 parts of hydrochloric acid of sp. gr. 1·18, till it dissolves, adding to the solution 41·95 parts of strychnine, and crystallising (Chiappero, *N. Br. Arch.* 115, 94). As the crystals thus obtained contain hydrochloric acid, (Ceresoli, *N. J. Pharm.* [4], 1, 343) dissolves 3·3 parts of arsenious acid in 3·12 parts of caustic potash and 40 parts of water; mixes the solution with a solution of 12 parts of strychnine in 20 parts of water and 2·65 parts of oil of vitriol; boils; filters the liquid hot, sulphate of potash being left behind; evaporates the filtrate; and exhausts the residue with absolute alcohol. — Dull white cubes, efflorescing in the air, having a bitter metallic taste, and without action on light. Soluble

in 35 parts of cold, and in 10 parts of boiling water, in alcohol, and less freely in ether (Ceresoli).

*Arseniate of Strychnine.* — $C^{42}N^2H^{22}O^4, 3HO, AsO^5 + HO$. An aqueous solution of the acid mixed with strychnine yields monoclinic prisms, soluble in 15 parts of cold, and in 5 parts of hot water, and with difficulty in alcohol and ether. — Forms with morphine a crystallisable double-salt, containing 1 atom of arsenious acid to each atom of base (Chiappero).

*Chlorozincate of Strychnine.* — A. *Anhydrous.* — A hot alcoholic solution of strychnine throws down hydrated oxide of zinc from an alcoholic solution of chloride of zinc, forming at the same time a double salt, which crystallises from the liquid after boiling for some time, filtering hot, and cooling. On adding hydrochloric acid to the boiling liquid, rendered cloudy by hydrated oxide of zinc and by strychnine thrown down at the same time, till it becomes clear, the whole solidifies, on cooling, to a crystalline mass of the same salt, which is to be washed with alcohol. — Pearly laminæ, composed of regular quadratic tables (Gräfinghoff).

| | *Dried in the air or at 100°.* | | | | Gräfinghoff. mean. |
|---|---|---|---|---|---|
| 42 C | | 252 | ........ | 57·47 | ........ | 57·37 |
| 2 N | | 28 | ........ | 6·39 | ........ | 6·21 |
| 23 H | | 23 | ........ | 5·25 | ........ | 5·27 |
| 4 O | | 32 | ........ | 7·30 | ........ | 7·57 |
| Zn | | 32·5 | ........ | 7·42 | ........ | 7·43 |
| 2 Cl | | 71 | ........ | 16·17 | ........ | 16·15 |
| $C^{42}N^2H^{22}O^4, HCl + ZnCl$ | .... | 438·5 | ........ | 100·00 | ........ | 100·00 |

B. *Hydrated.* — Obtained from the mother-liquor of A by spontaneous evaporation, or by mixing alcoholic hydrochlorate of strychnine with chloride of zinc, and leaving the solution to evaporate. — Transparent glassy prisms, which become cloudy at 130°, and lose 3·90 p. c. of water at 150° (2 at. = 3·94 p. c. HO) (Gräfinghoff, *J. pr. Chem.* 95, 229).

| | | | | | Gräfinghoff. mean. |
|---|---|---|---|---|---|
| 42 C | | ·252 | ........ | 55·21 | ........ | 55·20 |
| 2 N | | 28 | ........ | 6·14 | ........ | 6·10 |
| 25 H | | 25 | ........ | 5·47 | | |
| 6 O | | 48 | ........ | 10·52 | | |
| Zn | | 32·5 | ........ | 7·12 | ........ | 7·10 |
| 2 Cl | | 71 | ........ | 15·54 | ........ | 15·48 |
| $C^{42}N^2H^{22}O^4, HCl + ZnCl, 2HO$ | .... | 456·5 | ........ | 100·00 | | |

*Chlorocadmiate of Strychnine.* — $C^{42}N^2H^{22}O^4, HCl, CdCl$. — White glittering scales, long needles, or large transparent prisms. Does not lose water at 130°. Dissolves slightly in cold and hot water (Galletly, *Edin. New. Phil. J.* 4, 94; *Chem. Centr.* 1856, 607).

*Sulphate of Copper and Strychnine?* — By boiling an aqueous solution of sulphate of copper with strychnine, a pale-green liquid is obtained, yielding very long needles on evaporation (Pelletier & Caventou).

Strychnine decolorises ammoniacal sulphate of copper on boiling,

and forms crystals of a compound of strychnine and cupric oxide containing a little ammonia (Horsley).

*Iodomercurate of Strychnine.* — Iodomercurate of potassium throws down from strychnine-salts a dense white precipitate insoluble in hydrochloric acid (v. Planta; De Vrij). The precipitate is yellowish-white and remains amorphous (Delffs). By mixing solutions of 1 at. hydrochlorate of strychnine, 3 at. iodide of potassium, and 1 at. chloride of mercury, shining microscopic crystals are obtained, having the composition $C^{42}N^2H^{22}O^4,HI + 2HgI$. The crystals are insoluble in cold and in hot water, and but little soluble in boiling alcohol (Groves, *Chem. Soc. Qu. J.* 11, 97; *Chem. Centr.* 1858, 890).

*Bromomercurate of Strychnine* is obtained in the same way as the iodine-compound, by substituting bromide for iodide of potassium (Groves).

*Strychnine with Mercuric chloride.* Mercuric chloride throws down from a solution of strychnine in weak alcohol, a white crystalline precipitate, insoluble in water, alcohol, and ether (Nicholson & Abel).

|  |  |  |  |  | Nicholson & Abel. |
|---|---|---|---|---|---|
| 42 C | .......................... | 252 | ........ | 41·64 | ........ 41·52 |
| 2 N | .......................... | 28 | ........ | 4·63 | |
| 22 H | .......................... | 22 | ........ | 3·63 | ........ 3·77 |
| 4 O | .......................... | 32 | ........ | 5·29 | |
| 2 Cl | .......................... | 71 | ........ | 11·73 | ........ 11·74 |
| 2 Hg | .......................... | 200 | ........ | 33·08 | ........ 33·12 |
| $C^{42}N^2H^{22}O^4,2HgCl$ | .... | 605 | ........ | 100·00 | |

*Sulphate of Strychnine with Mercuric Chloride.* — Obtained in the form of a crystalline mass by dissolving the foregoing compound in sulphuric acid (Nicholson & Abel).

|  |  |  |  |  | Nicholson & Abel. |
|---|---|---|---|---|---|
| $C^{42}N^2H^{22}O^4$ | .......................... | 334 | ........ | 51·09 | |
| $HO,SO^3$ | .......................... | 49 | ........ | 7·49 | ........ 7·27 |
| $2HgCl$ | .......................... | 271 | ........ | 41·42 | |
| $C^{40}N^2H^{22}O^4,HO,SO^3 + 2HgCl$ | .... | 654 | ........ | 100·00 | |

Mercuric chloride throws down a precipitate from hydriodate of strychnine (Caillot).

*Chloromercurate of Strychnine.* — Mercuric chloride throws down from hydrochlorate of strychnine (and from the sulphate and nitrate after addition of chloride of sodium) a dense pulverulent precipitate, which soon turns gelatinous, and on addition of hydrochloric acid or sal-ammoniac, is converted (without dissolving) into a mass of needles (v. Planta). The salt is also formed by dissolving the compound of mercuric chloride and strychnine in hydrochloric acid. It dissolves with difficulty in water, but easily in alcohol, from which it crystallises (Nicholson & Abel).

|  |  |  |  |  | Nicholson & Abel. |
|---|---|---|---|---|---|
| 42 C | 252 | ........ | 39·27 | ........ | 39·28 |
| 2 N | 28 | ........ | 4·36 |  |  |
| 23 H | 23 | ........ | 3·58 | ... .... | 3·88 |
| 4 O | 32 | ........ | 4·98 |  |  |
| 3 Cl | 106·5 | ........ | 16·61 | ........ | 16·59 |
| 2 Hg | 200 | ........ | 31·20 | ........ | 31·38 |

$C^{42}N^2H^{22}O^4,HCl + 2HgCl$ .... 641·5 ........ 100·00

Strychnine forms a sparingly soluble compound with *mercurous nitrate* (Nicholson & Abel).

Alcoholic *nitrate of silver* throws down from alcoholic strychnine a crystalline compound containing equal numbers of atoms of nitric acid, oxide of silver, and strychnine (Regnault).

Strychnine forms a sparingly soluble compound with *protochloride of platinum* (Nicholson & Abel).

*Chloroplatinate of Strychnine.* — Bichloride of platinum throws down from hydrochlorate of strychnine, a yellowish-white precipitate (Robinet), nearly insoluble in water and ether, and soluble with difficulty in boiling alcohol, from which it crystallises in scales resembling mosaic gold. — Dissolves with decomposition in strong nitric acid (Nicholson & Abel), but not perceptibly in hydrochloric acid (v. Planta).

|  |  |  | Liebig. | Gerhardt. | Nicholson & Abel. *mean.* |
|---|---|---|---|---|---|
| 42 C | 252 | .... | 46·65 .... | .... 47·39 .... | 46·69 |
| 2 N | 28 | .... | 5·18 |  |  |
| 23 H | 23 | .... | 4·26 .... | .... 4·53 .... | 4·44 |
| 4 O | 32 | .... | 5·92 |  |  |
| Pt | 98·7 | .... | 18·27 |  |  |
| 3 Cl | 106·5 | .... | 19·72 .... | 17·82 .... 17·85 .... | 18·16 |

$C^{42}N^2H^{22}O^4,HCl,PtCl^2$ .... 540·2 .... 100·00

*Chloriridiate of Sodium* throws down from strychnine-salts a red-brown precipitate, not perceptibly soluble in hydrochloric acid (v. Planta).

*Chloropalladite of Strychnine.* — Protochloride of palladium throws down from hydrochlorate of strychnine, brown flocks, which dissolve in water and alcohol, and crystallise in dark-brown needles on cooling the solution (Nicholson & Abel).

|  |  |  | Nicholson & Abel. *mean.* |
|---|---|---|---|
| $C^{42}N^2H^{22}O^4,HCl,Cl$ | 406 | ........ | 88·41 |
| Pd | 53·3 | ........ | 11·59 ........ 11·50 |

$C^{42}N^2H^{22}O^4,HCl,PdCl$ ........ 459·3 ........ 100·00

*Chloroaurate of Strychnine.* — Thrown down by terchloride of gold from strychnine-salts as a lemon-yellow precipitate, which is very slightly soluble in water [insoluble in hydrochloric acid (v. Planta)], easily soluble in alcohol, but insoluble in ether (Larocque & Thibierge). The precipitate deposits gold in boiling water, and crystallises from alcohol in pale orange-coloured crystals (Nicholson & Abel).

| | at 100°. | | | | Nicholson & Abel. mean. |
|---|---|---|---|---|---|
| 42 C | 252 | ........ | 37·41 | ........ | 37·33 |
| 2 N | 28 | ........ | 4·15 | | |
| 22 H | 22 | ........ | 3·42 | ........ | 3·55 |
| 4 O | 32 | ........ | 4·75 | | |
| Au | 196·7 | ... .... | 29·19 | ........ | 29·15 |
| 4 Cl | 142 | ........ | 21·08 | | |

$C^{42}N^2H^{22}O^4,HCl,AuCl^3$ .... 672·7 ........ 100·00

*Hydrocyanate of Strychnine.* — The easily formed solution of strychnine in aqueous hydrocyanic acid leaves strychnine free from the acid when evaporated (Pelletier & Caventou).

*Hydroferrocyanate of Strychnine.* — A. *With* 1 *at. Ferrous Cyanide.* — This salt is deposited in nearly colourless needles on mixing cold saturated solutions of ferrocyanide of potassium and neutral salts of strychnine. More dilute solutions yield pale-yellow, rectangular, four-sided prisms, the ends of which are formed by two faces inclined to the edges of the prism. Hygroscopic. — The salt dissolves slightly in cold water and alcohol, and more freely in the hot liquids. The aqueous solution, on boiling, deposits strychnine, turns yellow, and yields crystals of hydroferrocyanate of strychnine. — Loses 6·12 p. c. of water at 100° (6 at. = 6·37 p. c.), and afterwards also hydrocyanic acid (Brandis).

| | Over chloride of calcium. | | | | Brandis. mean. |
|---|---|---|---|---|---|
| 90 C | 540 | ........ | 63·68 | ........ | 64·38 |
| 7 N | 98 | ........ | 11·56 | | |
| 54 H | 54 | ........ | 6·37 | ........ | 6·51 |
| 16 O | 128 | ........ | 15·09 | | |
| Fe | 28 | ........ | 3·30 | ........ | 3·36 |

$2(C^{42}N^2H^{22}O^4,HCy),FeCy + 8aq.$ .... 848 ........ 100·00

B. *With* 1 *at. Strychnine and* 2 *at. Ferrous Cyanide.* — The precipitate produced by alcoholic hydroferrocyanic acid in alcoholic solutions of strychnine-salts, dissolves at first on agitation, forming a clear solution which deposits the salt A; but when the hydroferrocyanic acid is added to acid reaction, the salt B is thrown down as an amorphous acid precipitate, which is to be washed with alcohol and water, and dried over oil of vitriol. This compound is also obtained by mixing hydroferrocyanic acid with hydroferricyanate of strychnine. — After drying it is permanent in the air, but in the moist state is easily decomposed, especially on warming, with formation of free hydrocyanic acid, a blue precipitate, and hydroferricyanate of strychnine. It is slowly decomposed by acids, with separation of Prussian blue, and by caustic potash, with formation of amorphous white flocks. — It is insoluble in water and alcohol. Loses 3·08 p. c. of water at 100° (2 at. = 3·5 p. c.) and then decomposes (Brandis).

| | Over oil of vitriol. | | | | Brandis. mean. |
|---|---|---|---|---|---|
| 48 C | 288 | ........ | 56·02 | ........ | 56·27 |
| 5 N | 70 | ........ | 13·62 | | |
| 28 H | 28 | ........ | 5·44 | ........ | 5·86 |
| 9 O | 72 | ........ | 14·03 | | |
| 2 Fe | 56 | ........ | 10·89 | ........ | 9·98 |

$C^{42}N^2H^{22}O^4,HCy,2FeCy + 5aq.$ ........ 514 ........ 100·00

Brandis supposes the salt to contain 1 at. more of hydrocyanic acid.   According to the above formula, it corresponds to ferrocyanide of iron and potassium (vii, 474).

*Hydroferricyanate of Strychnine.* — Obtained from the foregoing salt; also by boiling strychnine with water and Prussian blue, or by mixing hot saturated solutions of strychnine-salts and ferricyanide of potassium.   The free strychnine is removed by means of alcohol, and the salt is afterwards washed with cold water. — Small, very brilliant, golden-yellow prisms. — Extremely hygroscopic.   Dissolves very slightly in water and is decomposed by long boiling therewith, setting free hydrocyanic acid and throwing down oxide of iron and strychnine.   Potash and ammonia, added to the salt, precipitate strychnine; ferrous salts throw down Prussian blue.   Ferric salts form a clear blue solution, from which flocks of Prussian blue are gradually deposited. — The crystals lose in a vacuum over oil of vitriol, 1·82 p. c. water (3 at. = 2·04 p. c.), at 100°, altogether, 3·86 p. c. (6 at. = 4·06 p. c.), at 136°, 4·78 p. c. (8 at. = 5·43 p. c.) afterwards turning green and, at 200°, black (Brandis).

|  |  | *Crystals.* |  |  |  | Brandis. |
|---|---|---|---|---|---|---|
| 138 C | ............... | 828 | ........ | 62·48 | ........ | 63·23 |
| 12 N | ............... | 168 | ........ | 12·68 |  |  |
| 81 H | ............... | 81 | ........ | 6·11 | ........ | 6·38 |
| 24 O | ............... | 192 | ........ | 14·48 |  |  |
| 2 Fe | ............... | 56 | ........ | 4·25 | ........ | 4·11 |

3(C$^{42}$N$^2$H$^{20}$O$^4$,HCy) + Fe$^2$Cy$^3$ + 12aq.   ....   1325   ........   100·00
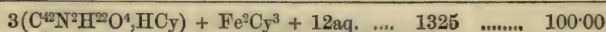
|  |  | *at 136°.* |  |  | Brandis. |  |
|---|---|---|---|---|---|---|
| 138 C | ............... | 828 | ........ | 66·08 |  |  |
| 12 N | ............... | 168 | ........ | 13·41 | ........ | 12·94 |
| 73 H | ............... | 73 | ........ | 5·83 |  |  |
| 16 O | ............... | 128 | ........ | 10·21 |  |  |
| 2 Fe | ............... | 56 | ........ | 4·47 | ........ | 4·44 |

3(C$^{42}$N$^2$H$^{20}$O$^4$,HCy) + Fe$^2$Cy$^3$ + 4aq.   ....   1253   ........   100·00
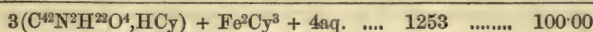
*Strychnine with Mercuric Cyanide.* — Precipitated from an alcoholic solution of strychnine by excess of mercuric cyanide. — Small prisms, slightly soluble in water and alcohol, insoluble in ether (Nicholson & Abel).

|  |  | at 100°. |  |  | Nicholson & Abel. |
|---|---|---|---|---|---|
| 46 C | ............... | 276 | ........ | 47·08 | ........ 46·96 |
| 4 N | ............... | 56 | ........ | 9·59 |  |
| 22 H | ............... | 22 | ........ | 3·75 | ........ 3·78 |
| 4 O | ............... | 32 | ........ | 5·46 |  |
| 2 Hg | ............... | 200 | ........ | 34·12 | ........ 34·16 |

C$^{42}$N$^2$H$^{22}$O$^4$,2HgCy   ....   586   ........   100·00
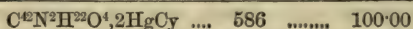
Hydriodate of strychnine is precipitated by *cyanide of mercury* (Caillot).

*Hydrochlorate of Strychnine with Mercuric Cyanide.* — A. *With* 1 *at. Mercuric Cyanide.* — On mixing hot very dilute aqueous solutions of hydrochlorate of strychnine and cyanide of mercury, a large quantity of needles is deposited after standing for a short time.   The needles are to be washed with water and alcohol in succession. —

Colourless well-formed crystals, soluble in hot water and alcohol (Kohl & Swoboda, *Wien. Acad. Ber.* 9, 252; *Ann. Pharm.* 83, 339).

| | Crystals. | | | | Nicholson & Abel. | | Kohl & Swoboda. |
|---|---|---|---|---|---|---|---|
| 44 C | 264 | ........ | 53·18 | ........ | 52·53 | ........ | 53·87 |
| 3 N | 42 | ........ | 8·46 | | | | |
| 23 H | 23 | ........ | 4·63 | ........ | | ........ | 4·72 |
| Cl | 35·5 | ........ | 7·13 | | | | |
| Hg | 100 | ........ | 20·14 | ........ | 20·20 | ........ | 19·72 |
| 4 O | 32 | ........ | 6·46 | | | | |
| $C^{42}N^2H^{22}O^4,HCl + HgCy$ | 496·5 | ........ | 100·00 | | | | |

B. *With 4 at. Mercuric Cyanide.* — Obtained by Brandis in the same manner as Nicholson & Abel afterwards obtained A. White, pearly, rectangular tables and prisms (Brandis).

| | Crystals. | | | | Brandis. |
|---|---|---|---|---|---|
| 50 C | 300 | ........ | 34·32 | ........ | 34·76 |
| 6 N | 84 | ........ | 9·60 | | |
| 23 H | 23 | ........ | 2·63 | | |
| Cl | 35·5 | ........ | 4·05 | | |
| 4 Hg | 400 | ........ | 45·74 | ........ | 45·25 |
| 4 O | 32 | ........ | 3·66 | | |
| $C^{42}N^2H^{22}O^4,HCl + 4HgCy$ | 874·5 | ........ | 100·00 | | |

*Hydroplatinocyanate of Strychnine.* — Platinocyanide of potassium throws down from an aqueous solution of nitrate of strychnine a copious white precipitate, which is quickly transformed into laminæ. — It crystallises from alcohol in short tufts of needles and four-sided prisms. — Dissolves easily in boiling alcohol. — Gives off its water of crystallisation at 120° (Schwarzenbach, *Pharm. Viertelj.* 8, 518).

| | Crystals. | | | | Schwarzenbach. |
|---|---|---|---|---|---|
| $C^{42}N^2H^{22}O^4,HCy^2$ | 387 | ........ | 76·84 | | |
| Pt | 98·7 | ........ | 19·59 | ........ | 19·41 |
| 2 HO | 18 | ........ | 3·57 | ........ | 3·5 |
| $C^{42}N^2H^{2\cdot}O^4,HCy,PtCy + 2aq.$ | 503·7 | ........ | 100·00 | | |

*Hydrosulphocyanate of Strychnine.* — Sulphocyanide of potassium, added to aqueous strychnine salts, throws down a dense crystalline precipitate, which disappears on heating, and again makes its appearance in long silky needles as the solution cools (Artus; v. Planta). The precipitate thrown down from dilute solutions of the hydrochlorate appears under a magnifying power of 250 diameters, as flat needles, truncated at one end, or terminated by an acute angle, sometimes isolated, sometimes united in irregular groups (Anderson, *N. J. Pharm.* 13, 443). Permanent in the air; neutral; of bitter and burning taste. Melts when gently warmed, solidifying on cooling, and leaves a porous charcoal when more strongly heated. The salt dissolves very slightly in cold water, but more easily in water at 70° (Artus); according to Lepage, it dissolves in cold water, but not in water containing sulphocyanide of potassium. It is very easily soluble in alcohol, and precipitable from the solution by water (Artus); insoluble in ether (Artus, *J. pr. Chem.* 3, 320; 8, 253. Henry, *J. Pharm.* 24, 194. Lepage, *J. Pharm.* 26, 140. Winckler, *Repert.* 53, 397).

Alcoholic strychnine and not too dilute hydrosulphocyanic acid yield transparent needles, which melt at 110° to 120° without losing weight (Dollfus, *Ann. Pharm.* 65, 215).

|  |  | Crystals. |  | Dollfus. |  |  |  | Nicholson & Abel. |
|---|---|---|---|---|---|---|---|---|
| 44 C | ............................... | 264 | ........ | 67·17 | ........ | 67·70 | ........ | 66·93 |
| 3 N | ............................... | 42 | ........ | 10·69 |  |  |  |  |
| 23 H | ............................... | 23 | ........ | 5·85 | ........ | 6·39 | ........ | 5·92 |
| 2 S | ............................... | 32 | ........ | 8·14 |  |  |  |  |
| 4 O | ............................... | 32 | ........ | 8·15 |  |  |  |  |
| C⁴²N²H²²O⁴,C²NHS³ | .... | 393 | ........ | 100·00 |  |  |  |  |

|  | Or : |  |  |  | Dollfus. |  | Nicholson & Abel. |
|---|---|---|---|---|---|---|---|
| C⁴²N²H²²O⁴ | .................... | 334 | ........ | 84·98 | ........ |  | ........ | 84·86 |
| C²NHS² | .................... | 59 | ........ | 15·02 | ........ | 14·45 | ........ | 14·96 |
| C⁴²N²H²²O⁴,C²NHS² | .... | 393 | ........ | 100·00 |  |  |  | 99·82 |

*Nitroprusside of Sodium* throws down crystalline precipitates from strychnine-salts (Neubauer, *Anal. Zeitschr.* 1, 515). It does not form precipitates, but colours the salts on evaporation (Werther, *J. pr. Chem.* 89, 498). See p. 486.

*Acetate of Strychnine.* — The neutral salt crystallises with difficulty, the acid salt easily (Pelletier & Caventou). — According to Abl, the salt dissolves in 96 parts of water, and according to Schlimpert (*N. Jahrb. Pharm.* 13, 248) in 15·1 parts of chloroform.

*Oxalate of Strychnine.* — A. *Neutral.* — Obtained by neutralising oxalic acid with strychnine (Nicholson & Abel). Formed also by boiling strychnine with aqueous parabanic acid, and cooling the filtrate, no oxalurate crystallising out (Elderhorst). — Long flat needles, neutral towards vegetable colours. Turns white at 100°, and loses 9·88 p. c. of water (9 at. = 9·65 p. c.) (Elderhorst, *Ann. Pharm.* 74, 83).

|  |  | at 100°. |  |  |  | Elderhorst. |
|---|---|---|---|---|---|---|
| 88 C | ........................ | 528 | ........ | 69·66 | ........ | 69·20 |
| 4 N | ........................ | 56 | ........ | 7·39 |  |  |
| 46 H | ........................ | 46 | ........ | 6·07 | ........ | 6·56 |
| 16 O | ........................ | 128 | ........ | 16·88 |  |  |
| 2C⁴²N²H²²O⁴,C⁴H²O⁸ | .... | 758 | ........ | 100·00 |  |  |

|  | Or : |  |  |  | Nicholson & Abel. |
|---|---|---|---|---|---|
| 2C⁴²N²H²²O⁴ | .... | 668 | ........ | 88·13 | ........ | 87·98 |
| C⁴H²O⁸ | .... | 90 | ........ | 11·87 | ........ | 11·86 |
| 2C⁴²N²H²²O⁴,C⁴H²O⁸ | .... | 758 | ........ | 100·00 | ........ | 99·84 |

B. *Acid.* — Obtained from A and free oxalic acid. Has an acid reaction (Nicholson & Abel).

|  |  |  |  |  | Nicholson & Abel. |
|---|---|---|---|---|---|
| C⁴²N²H²²O⁴ | .................... | 334 | ........ | 78·77 | ........ | 78·69 |
| C⁴H²O⁸ | .................... | 90 | ........ | 21·23 | ........ | 20·82 |
| C⁴²N²H²²O⁴,C⁴H²O⁸ | .... | 424 | ........ | 100·00 | ........ | 99·51 |

*Mellitate of Strychnine.* — Obtained by mixing an alcoholic solution

of strychnine with alcoholic mellitic acid, as a crystalline precipitate, which is dazzling-white and glittering when dry. — Crystallises from water in silky tufts of prisms. Gives off 1·2 p. c. of water at 100°, and 1·7 p. c. at 120°, and contains (dried ?) 20·39 p. c. of hypothetical anhydrous mellitic acid. — Soluble in 1,500 parts of cold, and in 650 parts of boiling water, but perfectly insoluble in alcohol (Karmrodt, *Ann. Pharm.* 81, 170).

*Tartrate of Strychnine.* — See p. 217. The strychnine-salts of tartaric and of antitartaric acid contain different proportions of water, and behave differently when heated; they have also different degrees of solubility (Pasteur).

A. *Dextrotartrate.* — a. *Neutral.* — The solution of 2 atoms of strychnine in 1 atom of bitartrate of potash yields fine crystals, which give off 14·3 p. c. of water at 100°, and no more below 170°. At 190° they become slightly coloured (Pasteur). On neutralising tartaric acid, or aqueous bitartrate of potash with strychnine, neutral shining needles an inch long are obtained. The needles effloresce in the air, become anhydrous at 130°, and dissolve easily in water and alcohol (Arppe, *J. pr. Chem.* 53, 331).

| | Crystals. | | | Arppe. | |
|---|---|---|---|---|---|
| $2C^{42}N^2H^{22}O^4,C^8H^6O^{12}$ ........................ | 818 | ........ | 91·91 | | |
| 8 HO ........................ | 72 | ........ | 8·09 | ........ 7·59 | ........ 7·76 |
| $2C^{42}N^2H^{22}O^4,C^8H^6O^{12}$ + 8aq. ......... | 890 | ......... | 100·00 | | |

7 at. water = 7·19 per cent. Pasteur's determination would correspond with 15 atoms of water (calc. 14·43 p. c.). — The dried salt contains 81·40 p. c. strychnine (calc. 81·66 p. c.) (Nicholson and Abel).

b. *Acid.* — Formed by dissolving strychnine in excess of tartaric acid. Slender shining needles, soluble in water. Permanent in the air: of acid reaction. According to Arppe, it loses the whole of its water of crystallisation at 125° [at 100° (Pasteur)], and nothing more below 170°, at which temperature, however, it becomes coloured. It remains transparent in absolute alcohol, without dissolving (Pasteur). This salt is formed, according to Nicholson & Abel, by boiling strychnine with solution of bitartrate of potash.

| | Needles. | | | Arppe. | Pasteur· |
|---|---|---|---|---|---|
| $C^{42}N^2H^{22}O^4$ ............................. | 334 | ........ | 62·08 | | |
| $C^8H^6O^{12}$ ............................. | 150 | ........ | 27·88 | | |
| 6HO ............................. | 54 | ........ | 10·04 | ........ 10·1 | ........ 10·3 |
| $C^{42}N^2H^{22}O^4,C^8H^6O^{12}$ + 6 aq. .... | 538 | ........ | 100·00 | | |

The anhydrous salt contains 68·74 p. c. of strychnine (calc. 69·00 p. c.) (Nicholson and Abel).

B. *Antitartrate of Strychnine.* — The *neutral* salt loses 7·8 per cent. of water at 100°, and nothing more at 200°, but becomes coloured at the latter temperature, though more slowly and to a less extent than the dextrotartrate. — The *acid* gives off *salt* the whole of its water of crystallisation, amounting to 10·3 p. c., at 100° more quickly than the corresponding dextrotartrate. It becomes coloured more slowly than the latter salt at 170°, and turns opaque in absolute alcohol (Pasteur, *N. Ann. Chim. Phys.* 38, 437).

*Tartrate of Antimony and Strychnine.* — Obtained in the same way as the corresponding quinidine-salt (p. 302). Lamellar tables or very brittle needles. Dissolves with difficulty in water (Stenhouse, *Ann. Pharm.* 129, 25).

|       |                                     | at 100° |        |        |        | Stenhouse. |
|-------|-------------------------------------|---------|--------|--------|--------|------------|
| 50 C  | ..............................      | 300     | ...... | 48·44  | ...... | 48·70      |
| 2 N   | ..............................      | 28      | ...... | 4·52   |        |            |
| 27 H  | ..............................      | 27      | ...... | 4·36   | ...... | 4·39       |
| 18 O  | ..............................      | 144     | ...... | 23·26  |        |            |
| Sb    | ..............................      | 120·3   | ...... | 19·42  | ...... | 19·62      |

C⁴²N⁴H²²O⁴,HO,SbO³,C⁸H⁴O¹⁰ .... 619·3  ...... 100·00

*Croconate of Strychnine* crystallises from alcohol in small yellow needles, soluble in water and alcohol. — *Rhodizonate of strychnine* is hyacinth-red, and soluble with reddish-yellow colour in water and alcohol (Heller).

*Picrate of Strychnine.* — Alcoholic picric acid throws down from alcoholic solutions of strychnine, a yellow precipitate, which crystallises from hot solutions, on cooling, in fine yellow crystals (Kemp, *Repert.* 71, 164).

*Picrotoxin* unites with strychnine (See under BRUCINE) (Pelletier & Couerbe).

*Hippurate of Strychnine.* — When excess of strychnine is boiled with a hot saturated solution of aqueous hippuric acid, the filtrate does not yield crystals on cooling; but when evaporated, it becomes syrupy, and afterwards forms a transparent amorphous mass, which in a few months turns hard and white, and then consists of microscopic needles collected in nodules (Elderhorst, *Ann. Pharm.* 74, 77).]

*Gallic acid* does not precipitate acetate of strychnine (Pfaff). — *Tannic acid* and tincture or infusion of galls throw down from salts of strychnine dense precipitates (Pfaff; Henry), which become denser on the addition of a little hydrochloric acid, and do not dissolve in a large quantity of the acid (v. Planta). — Strychnine behaves like quinine towards *oleic* and *margaric acids* (p. 294) (Attfield; Tripier). — It does not act upon *sugar*, *gum*, or *starch* (Pelletier & Caventou).

*Betuloretinate of Strychnine.* — Nitrate of strychnine throws down from the soda-salt of betuloretinic acid a precipitate, which turns crystalline during washing. The salt dissolves in alcohol, and remains as a yellow resin on evaporating the solution (Kösmann, *N. J. Pharm.* 26, 204).

Strychnine dissolves in 240 parts of *alcohol* of 20° B., but not in absolute alcohol (Merck). It is soluble in 120 parts of cold, and in 10 parts of boiling 80 p. c. alcohol (Wittstein). — It is insoluble in *ether* (Pelletier & Caventou). Soluble in 300 parts of *glycerin* (Cap & Garot). — According to M. Pettenkofer, it dissolves in 5 parts, according to Schlimpert, in 7 parts of *chloroform.* — It dissolves in *benzene* (Mansfield), in cold *picamar* and cold *creosote* (Reichenbach); easily in *volatile oils*, partly crystallising from a hot saturated solution on cooling (Pelletier & Caventou). — According to M. Pettenkofer, it dissolves in 100 parts, according to Cap & Garot, in 200 parts of *olive oil. Fat oils*, according to Pelletier & Caventou, dissolve only traces of it.

## Appendix to Strychnine.

*Strychnochromin.* — A resinous yellow colouring matter, from the lichens of false Angustura, also from those found on the bark of *Strychnos Pseudochina*, as well as from *Upas Tieuté*. — The lichens are exhausted with ether, and then with alcohol; the alcoholic tincture is evaporated; and the residue is boiled repeatedly with water, which dissolves extractive matters, and leaves the yellow. — Reddish-yellow, tasteless, non-poisonous powder. It dissolves in strong nitric acid with fine green colour, which disappears on diluting the solution with water, but appears again when the liquid is concentrated, and is turned yellow by hydrosulphuric acid, protochloride of tin, and ferrous sulphate. Strong nitric acid also throws down from alcoholic strychnochromin, a green precipitate which loses its colour when washed. — Oil of vitriol turns strychnochromin green; strong caustic potash decomposes it. — It is nearly insoluble in boiling water and dilute alkalis; soluble in acetic acid, from which it is precipitated by alkalis; easily soluble, with reddish-yellow colour in alcohol; and very slightly soluble in ether and volatile oils (Pelletier, *J. Pharm.* 5, 546; *N. Tr.* 4, 2, 221. Pelletier & Caventou, *Ann. Chim. Phys.* 26, 54).

The stychnine prepared from *Nux vomica*, *Faba St. Ignatii*, and *Upas Tieuté* obstinately retains a *yellow colouring matter*, which remains in solution when an aqueous extract of the Upas is precipitated with magnesia, and is obtained as a yellow extract on evaporation. This body is coloured bright red by strong nitric acid: it dissolves easily in water and alcohol, and is not precipitated by neutral acetate of lead (Pelletier & Caventou).

*Conjugated Compounds and Derivatives of Strychnine.*

# Oxystrychnine.

$$C^{42}N^2H^{28}O^{12}.$$
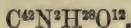
Schützenberger. *Compt. rend.* 47, 79; *Instit.* 1858, 239; *J. pr. Chem.* 75, 122; *Chem. Centr.* 1858, 677; *Ann. Pharm.* 108, 349; *Kopp's Jahresber.* 1858, 373.

An aqueous solution of sulphate of strychnine is boiled with nitrite of potash so long as nitrogen is evolved, and the pale-yellow liquid is precipitated with ammonia. A boiling alcoholic solution of the pale yellow flocks thus obtained deposits first yellow crystals of oxystrychnine and afterwards red crystals of bioxystrychnine.

Large orange-yellow, transparent, apparently rectangular prisms, truncated at the edges. Less bitter than strychnine. — Decomposes at 300°, without previous loss of water: melts when heated on platinum foil, and burns with a bright flame. — Soluble in alcohol, but not in water. The platinum double-salt contains 16·1 p. c. of platinum (calc. for $C^{42}N^2H^{28}O^{12}$,HCl,PtCl$^2$ requires 16·2 p. c. Pt).

|        |        | at 250°. |         |         | Schützenberger. |
|--------|--------|----------|---------|---------|-----------------|
| 42 C   | ...... | 252      | ....... | 62·37   | ........ | 62·50 |
| 2 N    | ...... | 28       | ....... | 6·93    | ........ | 7·05  |
| 28 H   | ...... | 28       | ....... | 6·93    | ........ | 7·05  |
| 12 O   | ...... | 96       | ....... | 23·77   | ........ | 23·40 |
| C⁴²N²H²⁸O¹² | .... | 404 | ........ | 100·00 | ........ | 100·00 |

## Bioxystrychnine.

### C⁴²N²H²⁸O¹⁴.
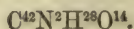
SCHÜTZENBERGER.    *Literature and Preparation* (p. 505).

Bitter orange-red prisms, which decompose at 300°, without previous loss of water. — Insoluble in water: soluble in alcohol more freely than oxystrychnine, and in ether. — The platinum double-salt contains 15·65 p.c. of platinum, corresponding to the formula C⁴²N²H²⁸O¹⁴, HCl,PtCl³ (by calc. 15·8 p.c. Pt).

|        |        |      |         |         | Schützenberger. |
|--------|--------|------|---------|---------|-----------------|
| 42 C   | ...... | 252  | ....... | 60·00   | ........ | 59·76 |
| 2 N    | ...... | 28   | ....... | 6·66    | ........ | 6·52  |
| 28 H   | ...... | 28   | ....... | 6·66    | ...... | 6·85  |
| 14 O   | ...... | 112  | ....... | 26·68   | ........ | 26·87 |
| C⁴²N²H²⁸O¹⁴ | .... | 420 | ........ | 100·00 | ........ | 100·00 |

## Methyl-strychnine.

### C⁴⁴N²H²⁴O⁴ = C⁴²N²H²¹(C²H³)O⁴.
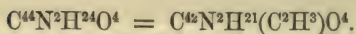
C. STAHLSCHMIDT.    *Pogg.* 108, 513; abstr. *Chem. Centr.* 1860, 196; *Répert. Chim. pure* 2, 135; *Kopp's Jahresber.* 1859, 395.

*Formestrychnin.* Known only in combination with water and acids.

Finely powdered strychnine is treated with a slight excess of iodide of methyl, the combination of the two bodies, which proceeds spontaneously at first, with evolution of heat, being completed by gently warming the mixture for some hours. The excess of methylic iodide is distilled off, and the residue dissolved in water, a little uncombined strychnine only remaining undissolved. The solution, on cooling, yields crystals of hydriodate of methyl-strychnine, from which the base may be separated by either of the following methods.

*a.* The hydriodate is agitated with 3 or 4 parts of cold water and with oxide of silver; the liquid is filtered from the iodide of silver thereby formed, and evaporated to a syrup, which deposits crystals of hydrate of methyl-strychnine. The dark mother-liquor, however, is no longer susceptible of crystallisation: it is better, therefore, to proceed as follows. — *b.* The hydriodate is decomposed with the proper quantity of sulphate of silver, and the solution is separated from iodide of silver, mixed with baryta-water, and evaporated to dryness. A solution of the residue yields on evaporation, crystals of hydrate of methyl-strych-

nine containing excess of water (see below), from which the normal *hydrate of methyl-strychnine* may be obtained by drying at 130° to 240°.

| | | *at 130° to 140°* | | | | | Stahlschmidt. |
|---|---|---|---|---|---|---|---|
| 44 C | ................................. | 264 | ........ | 72·13 | ........ | 71·79 to 73·07 |
| 2 N | ................................. | 28 | ........ | 7·65 | ........ | 7·01 „ 7·61 |
| 26 H | ................................. | 26 | ........ | 7·10 | ........ | 7·41 „ 7·67 |
| 6 O | ................................. | 48 | ........ | 13·12 | | |

$C^{42}N^2H^{21}(C^2H^3)O^4 + 2HO$ .... 366 ........ 100·00

Stahlschmidt considers the salt to contain 1 at. water less. His formula, $C^{44}N^2H^{25}O^5$, requires 73·96 p. c. C., 7·84 N., 7·00 H., and 11·20 O.

*Decompositions.* 1. Methyl-strychnine, when *heated*, evolves white vapours, melts, turns darker, and burns with smoky flame, leaving charcoal. — 2. It turns yellow and brown when heated with *oil of vitriol.* — 3. A solution of methyl-strychnine mixed with *bichromate of potash* throws down a brown-red precipitate on addition of one drop of dilute sulphuric acid, or acquires a blood-red to violet colour when more dilute. — 4. Methyl-strychnine is not perceptibly acted on by *chlorine.* — 5. It is not affected by *chlorate of potash* and oil of vitriol: water added to the mixture immediately colours it blood-red. — 6. The yellowish-red solution of methyl-strychnine in *nitric acid* becomes decolorised when heated, with liberation of nitric oxide and probably also of methylic nitrite : it throws down a large quantity of white flocks on addition of water, and assumes a dark red colour with protochloride of tin.

Aqueous methyl-strychnine (especially that obtained by decomposing the hydriodate with oxide of silver) acquires a dark wine-red to olive-green colour when evaporated, and deposits a black resin, which dissolves in acids with evolution of carbonic acid, forming an inky solution precipitable by caustic potash. When heated with strong nitric acid, it evolves nitric oxide and carbonic acid : the liquid deposits, on cooling, a brown mass, a solution of which in boiling water throws down a yellow powder as it cools. The same yellow powder is precipitated by water from the nitric acid mother-liquor : it dissolves in boiling water and alcohol, puffs up slightly when heated, turns brown and dissolves partially in caustic potash or ammonia, and is restored to its original colour by acids. Its solution in hydrochloric acid yields with bichloride of platinum a yellow precipitate containing, at 110°, 13·74 p. c. of platinum.

*Combinations.* — *With Water.* — *Hydrate of Methyl-strychnine.* — Yellowish, highly lustrous crystals, perfectly formed, and attaining a length of half an inch. Prismatic. Combination of $y$, $\alpha$, and $u$ (*fig.* 53); but with hemihedral development of the face $\alpha$. Angle $y : y$ before = 108° 50′; at the side = 71° 10′ (observed = 71° 15′); $u : u$ above = 94° 26′; at the side = 85° 34′ (observed = 85° 25′); $y : u = 113° 17′$ (observed = 113° 20′); $\alpha : y = 147° 50′$ (observed); $\alpha : u = 136° 30′$ (Rammelsberg, *Pogg.* 109, 378). Loses a part of its water of crystallisation at 100° and the rest at 135°. Does not taste bitter, and does not poison rabbits, when given to the extent of 11 grains in the course of a day. — It dissolves easily in water.

Hydrated methyl-strychnine forms with *acids* easily soluble salts, which generally crystallise well. Aqueous methyl-strychnine throws

down the oxides from salts of nickel, cobalt, iron, and copper; it likewise precipitates salts of alumina, and does not redissolve the precipitate when added in excess.

*Phosphate of Methyl-strychnine.* — Obtained by neutralising the aqueous base with phosphoric acid. — White crystalline mass, having a slightly acid reaction. Dissolves easily in water and alcohol. — Loses 7·66 p. c. of water at 130° (4 at. = 7·43 p. c. HO).

|  | | at 130°. | | | Stahlschmidt. |
|---|---|---|---|---|---|
| $C^{44}N^2H^{24}O^4,3HO$ | | 375 | ........ | 84·08 | |
| $PO^5$ | | 71 | ........ | 15·92 | ........ 17·10 |
| $C^{42}N^2H^{21}(C^2H^3)O^4,3HO,PO^5$ | .... | 446 | ........ | 100·00 | |

*Sulphate of Methyl-strychnine.* — A. *Neutral.* — Obtained by neutralising the aqueous base with dilute sulphuric acid, or by decomposing hydriodate of methyl-strychnine with sulphate of silver. It is deposited from the solution evaporated to a syrup in thin pearly laminæ. Dissolves easily in water. — The crystals effloresce in the air, and lose 10·26 p. c. of water at 100° (5 at. = 10·18 p. c.).

|  | | at 100°. | | | Stahlschmidt. |
|---|---|---|---|---|---|
| 44 C | | 264 | ........ | 66·49 | ........ 66·10 |
| 2 N | | 28 | ........ | 7·07 | |
| 25 H | | 25 | ........ | 6·29 | ........ 6·51 |
| 5 O | | 40 | ........ | 10·08 | |
| $SO^3$ | | 40 | ........ | 10·07 | ........ 9·95 |
| $C^{42}N^2H^{21}(C^2H^3)O^4,HO,SO^3$ | .... | 397 | ........ | 100·00 | |

B. *Acid.* — Crystallises more easily than A, after addition of free acid, in strongly acid laminæ. — Loses 3·61 p. c. of water at 100° (2 at. = 3·66 p. c.).

|  | | at 100° | | | Stahlschmidt. |
|---|---|---|---|---|---|
| $C^{44}N^2H^{24}O^4,2HO$ | | 366 | ........ | 82·06 | |
| 2 $SO^3$ | | 80 | ........ | 17·94 | ........ 18·62 |
| $C^{42}N^2H^{21}(C^2H^3)O^4,2(HO,SO^3)$ | .... | 446 | ........ | 100·00 | |

*Hydriodate of Methyl-strychnine.* — Fine pearly laminæ, soluble in 212 parts of cold, and easily in hot water. Dissolves with difficulty in alcohol.

|  | | Crystals. | | | Stahlschmidt. |
|---|---|---|---|---|---|
| 44 C | | 264 | ........ | 55·46 | ........ 55·10 |
| 2 N | | 28 | ........ | 5·88 | |
| 25 H | | 25 | ........ | 5·25 | ........ 5·81 |
| 4 O | | 32 | ........ | 6·74 | |
| I | | 127 | ........ | 26·67 | ........ 26·62 |
| $C^{42}N^2H^{21}(C^2H^3)O^4,HI$ | .... | 476 | ........ | 100·00 | |

*Hydrobromate of Methyl-strychnine.* — Bromide of potassium immediately throws down from a strong solution of the hydrochlorate, slender needles of this salt, sparingly soluble in cold, easily soluble in hot water and in alcohol.

|  | | Crystals. | | | Stahlschmidt. |
|---|---|---|---|---|---|
| $C^{44}N^2H^{24}O^4,H$ | | 349 | ........ | 81·35 | |
| Br | | 80 | ........ | 18·65 | ........ 18·5 |
| $C^{42}N^2H^{21}(C^2H^3)O^4,HBr$ | .... | 429 | ........ | 100·00 | |

*Hydrochlorate of Methyl-strychnine.* — Formed by neutralising the aqueous base with hydrochloric acid, or by decomposing the sulphate with chloride of barium. — Fine prisms, half an inch long, soluble in water and alcohol. — Effloresces over oil of vitriol, and loses 8·22 p. c. of water at 100° (4 at. = 8·56 p. c.).

| | | | at 100°. | | | Stahlschmidt. | |
|---|---|---|---|---|---|---|---|
| 44 C | ................................. | | 264 | ........ | 68·66 | ........ | 68·44 |
| 2 N | ................................. | | 28 | ........ | 7·29 | | |
| 25 H | ................................. | | 25 | ........ | 6·50 | ........ | 6·87 |
| 4 O | ................................. | | 32 | ........ | 8·32 | | |
| Cl | ................................. | | 35·5 | ........ | 9·23 | ........ | 9·10 |
| $C^{42}N^2H^{21}(C^2H^3)O^4,HCl$ | .... | | 384·5 | ........ | 100·00 | | |

*Nitrite of Methyl-strychnine.* — On decomposing the hydriodate with nitrite of silver and evaporating the solution, a radiated crystalline mass is obtained, which dissolves easily in water and alcohol, and evolves nitrous acid with acids. — When heated, the compound melts, puffs up, evolves acid vapours, and leaves a brown-black residue, insoluble in water, the easily formed alcoholic solution of which dries up to an asphalt-like mass, even after addition of hydrochloric acid.

*Nitrate of Methyl-strychnine.* — Slender needles, sparingly soluble in cold water, easily soluble in hot water and alcohol, insoluble in ether. — When heated, the salt turns yellow, melts, puffs up, and burns with luminous flame, leaving charcoal.

| | | at 100°. | | | Stahlschmidt. | |
|---|---|---|---|---|---|---|
| 44 C | ................................. | 264 | ........ | 64·23 | ........ | 63·71 |
| 3 N | ................................. | 42 | ........ | 10·22 | ........ | 10·81 |
| 25 H | ................................. | 25 | ........ | 6·08 | ........ | 6·22 |
| 10 O | ................................. | 80 | ........ | 19·47 | ........ | 19·26 |
| $C^{42}N^2H^{21}(C^2H^3)O^4,HO,NO^5$ | .... | 411 | ........ | 100·00 | ........ | 100·00 |

*Chromate of Methyl-strychnine.* — Neutral chromate of potash throws down from the hydrochlorate, a red-brown precipitate, which is deposited from its solution in boiling water, as it cools, in the form of a powder.

*Chloromercurate of Methyl-strychnine.* — The white precipitate thrown down by mercuric chloride from hydrochlorate of methyl-strychnine, dissolves slightly in cold water and alcohol, and crystallises from a hot solution in tufts of needles on cooling.

| | | at 100°. | | | Stahlschmidt. |
|---|---|---|---|---|---|
| $C^{44}N^2H^{24}O^4,HCl,5Cl$ | ...................... | 566 | ........ | 53·09 | |
| 5 Hg | .................................. | 500 | ........ | 46·91 | ........ 46·65 |
| $C^{42}N^2H^{21}(C^2H^3)O^4,HCl + 5HgCl$ | .... | 1066 | ........ | 100·00 | |

*Chloroplatinate of Methyl-strychnine.* — Pale-yellow precipitate, soluble with difficulty in water and alcohol, insoluble in ether. Contains, at 100°, 17·57 p. c. of platinum (calc. 17·81 p. c.).

*Chloroaurate of Methyl-strychnine.* — Pale-yellow precipitate, crystallising from solution in hot water or alcohol in orange-coloured tufts of needles. Decomposes on long boiling, with separation of gold. Con-

tains, at 100°, 28·68 p. c. of gold (calc. for C$^{42}$N$^2$H$^{21}$(C$^2$H$^3$)O$^4$,HCl,AuCl$^3$, 28·59 p. c. Au).

*Hydroferrocyanate of Methyl-strychnine.* — Ferrocyanide of potassium throws down from a solution of hydrochlorate of methyl-strychnine mixed with a little hydrochloric acid, a yellow precipitate which crystallises from a solution in boiling water. On long boiling or by prolonged contact with hydrochloric acid, the precipitate is decomposed, with separation of Prussian blue. After drying at 100°, it contains 6·2 p. c. of iron, corresponding to the formula C$^{42}$N$^2$H$^{21}$(C$^2$H$^3$)O$^4$,2HCy + FeCy (calc. 6·14 p. c. Fe).

*Ferricyanide of potassium* throws down from hydrochlorate of methyl-strychnine, a white precipitate, which crystallises from hot water in small shining prisms, and is insoluble in alcohol.

*Acetate* and *Oxalate of Methyl-strychnine* are easily soluble and crystallise with difficulty.

Methyl-strychnine dissolves easily in *alcohol*, but very slightly in *ether*.

## Ethylstrychnine.

$$C^{46}N^2H^{26}O^4 = C^{40}N^2(C^4H^5)H^{19}O^4,H^2.$$
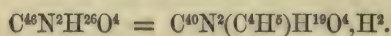
H. How. *Trans. Roy. Soc. Edin.* 21, 1, 27; *Chem. Gaz.* 1854, 321, 341 and 365; *Ann. Pharm.* 92, 326; *J. pr. Chem.* 63, 300; *Pharm. Centr.* 1855, 26; *Kopp's Jahresber.* 1854, 514.

*Vinestrychnin.* Known only as hydrate and in combination with acids. The hydrate may be regarded as analogous to hydrated oxide of ammonium.

When strychnine is heated to 100° with iodide of ethyl and alcohol for 20 minutes in a sealed tube, and the hydriodate of ethylstrychnine thereby formed is decomposed by moist oxide of silver, a purple-red solution containing ethylstrychnine is obtained. The solution is allowed to evaporate spontaneously without exposure to carbonic acid; the red crystalline residue is dissolved in a little water and filtered from the flocks which separate; and after again evaporating in a vacuum, the residue is dissolved in hot anhydrous alcohol, from which small colourless prisms of hydrate of ethylstrychnine crystallise as it cools. Or the base may be precipitated from the alcoholic solution by ether, in the form of a jelly, which soon becomes crystalline. — It is bitter, and has an alkaline reaction.

|        |     | *In vacuo.* |     |       |     | How. |
|--------|-----|-------------|-----|-------|-----|------|
| 46 C   | ..............................  | 276 | ....... | 67·81 | ....... | 68·13 |
| 2 N    | ..............................  | 28  | ....... | 6·88  |         |      |
| 31 H   | ..............................  | 31  | ....... | 7·61  | ....... | 8·19 |
| 9 O    | ..............................  | 72  | ....... | 17·70 |         |      |
| C$^{42}$N$^2$H$^{21}$(C$^4$H$^5$)O$^4$,HO + 4aq. | .... | 407 | ....... | 100·00 |     |      |

The crystals do not lose water at 100°, but decompose at *a higher temperature*. When heated with *iodide of ethyl*, they form hydriodate of ethylstrychnine, and, if alcohol is present, also a basic product. The *aqueous solution* of the crystals is purple-red: it evolves an odour of

volatile bases when *boiled*. The crystals give the strychnine reaction with oil of vitriol and bichromate of potash.

Aqueous ethylstrychnine combines with *acids*, generally even when in combination with bases, precipitating the oxides. It precipitates the chlorides of calcium and barium only when heated, but decomposes the salts of the heavy metals, sulphate of magnesia, and sulphate of alumina, even in the cold.

*Carbonate of Ethylstrychnine.* — The aqueous solution of the base absorbs carbonic acid from the air.

A. *Neutral.* — When moist carbonate of silver is agitated with hydriodate of ethylstrychnine and water, a colourless solution, free from iodine, is obtained. The solution acquires a yellow colour if allowed to stand over the precipitate. When evaporated in a vacuum or at 100°, it leaves a crystalline residue, from which water takes up carbonate of ethylstrychnine, leaving white flocks of a new base undissolved.

B. *Acid.* — Formed by passing carbonic acid into the solution obtained according to A, and evaporating the filtrate in a vacuum or at 100°. — White crystalline mass, not deliquescent, and having an alkaline reaction. — Dissolves easily in water and in absolute alcohol, and is precipitated from the latter solution in colourless prisms by ether.

|  |  |  |  | How. mean. |
|---|---|---|---|---|
| $C^{46}N^2H^{26}O^4,2HO$ | 380 | ........ | 89·62 | — |
| $2CO^2$ | 44 | ........ | 10·38 | 10·53 |
| $C^{42}N^2H^{21}(C^4H^5)O^4,2(HO,CO^2)$ | 424 | ........ | 100·00 | |

A solution of ethylstrychnine saturated with hydrosulphuric acid and exposed to the air, becomes converted into *hyposulphite*, which may be obtained in crystals.

*Sulphate of Ethylstrychnine.* — The neutral salt in water dissolves less easily than the hydrochlorate; the solution, supersaturated with sulphuric acid, yields pearly needles and flocks, probably of an acid salt.

*Hydriodate of Ethylstrychnine.* — Shining, white, four-sided prisms or needles, which do not lose weight at 100°, and at a higher temperature melt, carbonise, and give off repulsive alkaline vapours, condensing to a yellow oil. — The salt dissolves in 170 parts of water at 15° in 50 or 60 parts of boiling water, and less freely in ammonia-water and caustic potash, so that these liquids throw down the salt from its aqueous solution. — Soluble in alcohol. — When distilled with carbonate of soda, it yields a heavy oil, only partially soluble in acids.

|  |  | Crystals. |  |  | How. |
|---|---|---|---|---|---|
| 46 C | ........ | 276 | ........ | 56·31 | 56·27 |
| 2 N | ........ | 28 | ........ | 5·71 | |
| 27 H | ........ | 27 | ........ | 5·50 | 5·60 |
| I | ........ | 127 | ........ | 25·93 | 25·98 |
| 4 O | ........ | 32 | ........ | 6·55 | |
| $C^{42}N^2(C^4H^5)H^{21}O^4,HI$ | | 490 | ........ | 100·00 | |

*Hydrochlorate of Ethylstrychnine* forms easily soluble needles.

*Nitrate of Ethylstrychnine.* — Formed from the hydriodate and nitrate of silver. — Colourless, highly refractive prisms, very slightly soluble in cold, easily soluble in boiling, water.

|  |  | Crystals. |  |  |  | How. |
|---|---|---|---|---|---|---|
| 46 C | ............................... | 276 | ........ | 64·94 | ........ | 64·60 |
| 3 N | ............................... | 42 | ........ | 9·88 | | |
| 27 H | ............................... | 27 | ........ | 6·35 | ........ | 6·53 |
| 10 O | ............................... | 80 | ........ | 18·83 | | |
| C⁴²N²H²¹(C⁴H⁵)O⁴,HO,NO⁵ | .... | 425 | ........ | 100·00 | | |

*Chromate of Ethylstrychnine.* — The neutral salt, obtained by double decomposition, forms short yellow prisms. — *Acid salt.* — Golden-yellow, transparent tables, or tufts of needles, obtained by double decomposition. — Dissolves slightly in cold, easily in boiling water. — Loses 3·60 p. c. (= 2 at.) of water at 100°.

|  |  | Dried. |  |  |  | How. mean. |
|---|---|---|---|---|---|---|
| 46 C | ............................... | 276 | ........ | 57·33 | ........ | 57·15 |
| 2 N | ............................... | 28 | ........ | 5·81 | | |
| 28 H | ............................... | 28 | ........ | 5·81 | ........ | 5·91 |
| 6 O | ............................... | 48 | ........ | 9·99 | | |
| 2 CrO³ | ............................... | 101·4 | ........ | 21·06 | ........ | 20·87 |
| C⁴²N²H²¹(C⁴H⁵)O⁴,2(HO,CrO³) | .... | 481·4 | ........ | 100·00 | | |

*Mercuric chloride* throws down from hydrochlorate of ethylstrychnine, a white precipitate which crystallises from hot water in needles. — *Chloroaurate of ethylstrychnine* forms colourless shining prisms.

*Chloroplatinate of Ethylstrychnine.* — Yellow precipitate, becoming crystalline after a few hours. Dilute solutions yield stellate groups of crystals.

|  |  | Crystals. |  |  |  | How. |
|---|---|---|---|---|---|---|
| C⁴⁶N²H²⁶O⁴,HCl³ | ........................ | 469·5 | ........ | 82·63 | | |
| Pt | ................................... | 98·7 | ........ | 17·37 | ........ | 17·46 |
| C⁴²N²H²¹(C⁴H⁵)O⁴,HCl,PtCl² | .... | 568·2 | ........ | 100·00 | | |

*Acetate of Ethylstrychnine* remains behind in the form of a gum on evaporating its aqueous solution.

# Compounds obtained from Strychnine and Bibromide of Ethylene.

MÉNÉTRIÈS. *N. Petersb. Acad. Bull.* 4, 570; *J. pr. Chem.* 85, 230; *Chem. Centr.* 1862, 145; *Kopp's Jahresber.* 1861, 542.

When strychnine is heated to 100° for a quarter of an hour with alcohol and excess of bibromide of ethylene in a sealed tube, white crystals are formed, which may be freed from excess of the bibromide and alcohol by heat, and allowed to crystallise from water.

The crystals are *bihydrobromate of ethylene-strychnine* or, according to Ménétriès, *bromide of strychnine-bromethyl.* They dissolve slightly in

cold, and easily in hot water and alcohol, are not precipitated by ammonia or aqueous alkalis, and exhibit the reactions of strychnine with oil of vitriol and bichromate of potash.

| | | | *Crystals.* | | | *Ménétriès. mean.* |
|---|---|---|---|---|---|---|
| 46 C | .................................... | 276 | ........ | 52·87 | ........ | 52·68 |
| 2 N | .................................... | 28 | ........ | 5·36 | | |
| 26 H | .................................... | 26 | ........ | 4·98 | ........ | 5·05 |
| 4 O | .................................... | 32 | ........ | 6·13 | | |
| Br | .................................... | 80 | ........ | 15·33 | ........ | 15·48 |
| Br | .................................... | 80 | ........ | 15·33 | | |
| $C^{42}N^2H^{20}(C^4H^4)O^4,2HBr$ | ........ | 522 | ........ | 100·00 | | |

In contact with silver-salts, the crystals give up half their bromine, and in contact with moist oxide of silver, the whole of the bromine, as bromide of silver, thus forming two distinct series of compounds.

### A. *Compounds containing Bromine.*

When the crystals are decomposed by sulphate of silver, and the filtrate is freed from excess of silver and of sulphuric acid by baryta-water, and afterwards treated with carbonic acid and filtered, an alkaline liquid is obtained, which leaves on evaporation a resin represented by the formula $C^{42}N^2H^{21}(C^4H^4Br)O^4$, 2HO., the *hydrated oxide of strychnine-bromethylammonium* of Ménétriès.

*Sulphate.* — $C^{42}N^2H^{21}(C^4H^4Br)O^4,2(HO,SO^3)$. Obtained from sulphate of silver and bihydrobromate of ethylene-strychnine.

*Nitrate.* — Delicate white needles, sparingly soluble in cold, easily soluble in hot water, not decomposible by ammonia or caustic potash. — By evaporation with an excess of nitric acid, it is converted into a pale-yellow crystalline nitro-compound.

| | | | | | | *Ménétriès.* |
|---|---|---|---|---|---|---|
| 46 C | .................................... | 276 | ........ | 54·76 | ........ | 54·62 |
| 3 N | .................................... | 42 | ........ | 8·34 | | |
| 26 H | .................................... | 26 | ........ | 5·16 | ........ | 5·27 |
| 10 O | .................................... | 80 | ........ | 15·87 | | |
| Br | .................................... | 80 | ........ | 15·87 | | |
| $C^{42}N^2H^{21}(C^4H^4Br)O^4,HO,NO^5$ | .... | 504 | ........ | 100·00 | | |

*Platinum-salt.* — Chloride of platinum throws down from the hydrochlorate (which crystallises with difficulty) a pale orange-yellow precipitate.

| | | | | | *Ménétriès.* |
|---|---|---|---|---|---|
| $C^{42}N^2H^{21}(C^4H^4Br)O^4,HCl,Cl^2$ | ........ | 548·5 | ........ | 84·75 | |
| Pt | .............................. | 98·7 | ........ | 15·25 | ........ 15·24 |
| $C^{42}N^2H^{21}C^4H^4BrO^4,HCl,PtCl^2$ | .... | 647·2 | ........ | 100·00 | |

### B. *Compounds free from Bromine.*

A solution of bihydrobromate of ethylene-strychnine assumes a wine-red colour when digested with excess of moist oxide of silver, and leaves, on evaporation of the filtrate, white alkaline *hydrate of*

*ethylene-strychnine*, $C^{42}N^2H^{20}(C^4H^4)O^4$, 2HO, which dissolves easily in water. Chlorine passed into the aqueous solution of this substance forms (1) *trichlor-ethylene-strychnine*, $C^{42}N^2H^{17}Cl^3(C^4H^4)O^4$, a white frothy body which dissolves in alcohol and ether, and carbonises at 160°, with liberation of hydrochloric acid; and (2) a base precipitable from the concentrated solution by chloride of platinum, probably $C^{42}N^2H^{19}Cl(C^4H^4)O^4$. — When an aqueous solution of hydrate of ethylene-strychnine is mixed with nitric acid, the liquid deposits first a white crystalline powder, insoluble in water, but soluble in strong acids, and afterwards, on evaporating with nitric acid, an orange-red body, which explodes when heated, probably *nitrate of nitro-ethylene-strychnine* $C^{42}N^2H^{19}X(C^4H^4)O^4,HO,NO^5$.

Hydrate of ethylene-strychnine is not precipitable by ammonia or caustic potash. It produces with iodide of potassium a white precipitate; with protochloride of tin a white precipitate, insoluble in excess of the tin-salt; with mercuric chloride a white crystalline compound. — The acid sulphate, $C^{42}N^2H^{20}(C^4H^4)O^4,2(HO,SO^3)$, is crystallisable. The easily soluble hydrochlorate contains 9·1 p. c. chlorine, corresponding to the formula $C^{42}N^2H^{20}(C^4H^4)O^4,HCl$ (calc. 8·99 p. c. Cl): it produces a pale orange-yellow precipitate with bichloride of platinum.

*Chromate.* — Bichromate of potash throws down a yellow precipitate from aqueous hydrate of ethylene-strychnine.

|  |  |  |  |  | Ménétriès. |
|---|---|---|---|---|---|
| 46 C | ............ | 276 | ........ | 57·57 | ........ 57·74 |
| 2 N | ............ | 28 | ........ | 5·85 | |
| 26 H | ............ | 26 | ........ | 5·42 | ........ 5·90 |
| 6 O | ............ | 48 | ........ | 10·01 | |
| 2CrO³ | ............ | 101·4 | ........ | 21·15 | ........ 20·96 |
| $C^{42}N^2H^{20}(C^4H^4)O^4,2(HO,CrO^3)$ | | 479·4 | ........ | 100·00 | |

## Amylstrychnine.

$$C^{52}N^2H^{32}O^4 = C^{42}N^2(C^{10}H^{11})H^{21}O^4.$$
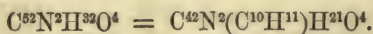
H. How. *Trans. Roy. Soc. Edin.* 21, 1, 27; *Ann. Pharm.* 92, 326.

*Mylestrychnin.*

When finely powdered strychnine is heated to 100° with absolute alcohol and chloride of amyl for 100 hours in a sealed tube, an oily body is formed, which solidifies to a crystalline mass when the alcohol and excess of amylic chloride are evaporated. An aqueous solution of the hydrochlorate of amylstrychnine thus obtained, when decomposed by moist oxide of silver, yields an alkaline purple-coloured solution of amylstrychnine, which behaves like the corresponding ethyl-compound.

*Hydrochlorate of Amylstrychnine.* — Colourless oblique rhombic prisms. Precipitated unaltered from the aqueous solution after some time by ammonia, and immediately by caustic potash. Prolonged heating to 100° with ammonia in a sealed tube decomposes it, strychnine and other products being apparently formed. — It loses 12·54 p. c. of water at 100° (7 at. = 12·29 p. c.), still retaining 1 atom.

|        |        | *at* 100°. |        |        |        | How.  |
|--------|--------|-----------|--------|--------|--------|-------|
| 52 C   | ...... | 312       | ...... | 69·41  | ...... | 69·37 |
| 2 N    | ...... | 28        | ...... | 6·24   |        |       |
| 34 H   | ...... | 34        | ...... | 7·56   | ...... | 7·84  |
| 5 O    | ...... | 40        | ...... | 8·90   |        |       |
| Cl     | ...... | 35·5      | ...... | 7·89   | ...... | 8·03  |

| $C^{42}N^2(C^{10}H^{11})H^{21}O^4,HCl + aq.$ | .... | 449·5 | ...... | 100·00 |
|---|---|---|---|---|

*Nitrate of Amylstrychnine.* — Radiated groups of colourless needles, which give off 15·90 p. c. of water at 100° (10 at. = 15·9 p. c.), still retaining 1 atom.

|        |        | *at* 100°. |        |        |        | How.  |
|--------|--------|-----------|--------|--------|--------|-------|
| 52 C   | ...... | 312       | ...... | 65·54  | ...... | 65·32 |
| 3 N    | ...... | 42        | ...... | 8·82   |        |       |
| 34 H   | ...... | 34        | ...... | 7·14   | ...... | 7·26  |
| 11 O   | ...... | 88        | ...... | 18·50  |        |       |

| $C^{42}N^2H^{21}(C^{10}H^{11})O^4,HO,NO^5 + aq$ | .... | 476 | ...... | 100·00 |
|---|---|---|---|---|

*Chromate of Amylstrychnine.* — Yellow crystals, soluble in boiling water.

|        |        | *at* 100° |        |        |        | How.  |
|--------|--------|-----------|--------|--------|--------|-------|
| $C^{52}N^2H^{32}O^4,2HO$ | ...... | 422·0 | ...... | 80·63 |       |       |
| 2 $CrO^3$ | ...... | 101·4 | ...... | 19·37 | ...... | 19·63 |

| $C^{42}N^2H^{21}(C^{10}H^{11})O^4,2(HO,CrO^3)$ | .... | 523·4 | ...... | 100·00 |
|---|---|---|---|---|

Hydrochlorate of amylstrychnine forms with *mercuric chloride* a white sparingly soluble double-salt, which crystallises from boiling water. — It produces with *terchloride of gold* a yellow amorphous precipitate ; and with *bichloride of platinum* a pale-yellow crystalline compound of varying composition.

Oxychlorazo-nucleus $C^{42}N^2ClH^{19}O^4$.

## Chlorostrychnine.

$$C^{42}N^2ClH^{21}O^4 = C^{42}N^2ClH^{19}O^4,H^2.$$
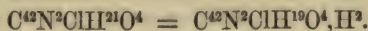
LAURENT. *Compt. rend.* 24, 220 ; *N. Ann. Chim. Phys.* 24, 313 ; *Ann. Pharm.* 69, 14 ; *J. pr. Chem.* 46, 52.

A hot solution of hydrochlorate of strychnine assumes a rose-red colour when a current of chlorine gas is passed into it [on account of the presence of brucine (Pelletier)], and after some time deposits a resin, whilst the solution contains hydrochlorate of chlorostrychnine. On adding ammonia to the solution, drop by drop, till a slight permanent precipitate is produced, and filtering the liquid, the chlorostrychnine is thrown down from the filtrate as a white precipitate, which must be washed on the filter.

Chlorostrychnine, neutralised with dilute sulphuric acid and evaporated, yields crystals of sulphate.

|  | Crystals. |  |  |  | Laurent. |
|---|---|---|---|---|---|
| $C^{42}N^2H^{21}O^4,HO$ ............................ | 342 | ........ | 71·20 |  |  |
| Cl ........................................ | 35·5 | ........ | 7·39 | ........ | 7·30 |
| $SO^3$......................................... | 40 | ........ | 8·31 | ........ | 8·58 |
| 7 HO.......................................... | 63 | ...... | 13·10 | ........ | 13·00 |

$C^{42}N^2H^{21}ClO^4,HO,SO^3 + 7HO$  ....  480·5  ........  100·00

Pelletier's *chlorostrychnin* (see p. 485) differs from the above. It is obtained by completely decomposing a solution of strychnine in 100 parts of water with chlorine, washing the white mass thereby thrown down with cold and boiling water, and dissolving it in ether, which leaves shining white laminæ on evaporation. The body tastes bitter, though less bitter than strychnine; it evolves hydrochloric acid and carbonises at 150°; is nearly insoluble in water, only slightly soluble in acidulated water, and does not combine with acids. It crystallises from its easily formed solution in alcohol in microscopic needles. Contains 47·76 p. c. C., 5·19 N., 4·37 H., 24·57 Cl., and 18·11 O (Pelletier). See also Regnault (*Ann. Pharm.* 29, 62), who doubts the purity of this product, having found in chlorostrychnine the same quantity of carbon and hydrogen as Pelletier, but a larger proportion of chlorine.

*Primary Nucleus* C⁴²H³⁰; *Oxygen-nucleus* C⁴²H²²O⁶.

## Scoparin.

$$C^{42}H^{22}O^{10} = C^{42}H^{22}O^8,O^2.$$
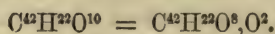
STENHOUSE. *Ann. Pharm.* 78, 15; *Phil. Trans.* 1851, 422; abstr. *Chem. Soc. Qu. J.* 4, 216; *Pharm. Centr.* 1851, 437 : *Lieb. Kopp's Jahresber.* 1851, 570.

*Source.* In *Spartium Scoparium*, together with spartëine (xiii, 152, and xvi, 282). — Reinsch obtained from the same plant a bitter substance (*Jahrb. pr. Pharm.* 12, 141).

*Preparation.* The decoction obtained by boiling the plant for six or eight hours with water, when evaporated to $\frac{1}{10}$th of its bulk, and left at rest for 24 hours, solidifies to a jelly containing scoparin, together with chlorophyll and a little spartëine. The jelly is washed with a little cold water, dissolved in boiling water containing a few drops of hydrochloric acid, filtered, and set aside till it solidifies; and the jelly again formed is purified by washing, pressing, drying in a water-bath, and dissolving in boiling water, which now leaves most of the chlorophyll undissolved. The chlorophyll may also be precipitated from the aqueous solution by long continued boiling; it is deposited from a moderately concentrated solution before the scoparin, and may be separated by filtration at the proper point.

Scoparin thus obtained forms, after drying in a vacuum, a pale-yellow, brittle, amorphous mass, which is tasteless, inodorous, and neutral. By precipitating its cold ammoniacal solution with hydrochloric acid, dissolving the somewhat more solid jelly in boiling water, and cooling slowly, a small quantity of pale-yellow crystalline stars is obtained, together with gelatinous scoparin. The solution in hot alcohol likewise yields a jelly on partial evaporation, and also crystals in the cold. When an attempt is made to recrystallise the latter from hot alcohol, there remains a residue which dissolves with difficulty in

water and alcohol, and is obtained as a jelly having the original degree of solubility only by dissolving it in ammonia-water, and precipitating with hydrochloric acid.

The crystals and the jelly have the same composition after drying.

|  | | In a vacuum or at 100°. | | | Stenhouse. mean. |
| --- | --- | --- | --- | --- | --- |
| 42 C | ............ | 252 | ............ | 58·06 | ............ | 57·67 |
| 22 H | ............ | 22 | ............ | 5·06 | ............ | 5·35 |
| 20 O | ............ | 160 | ............ | 36·88 | ............ | 36·98 |
| $C^{42}H^{22}O^{20}$ | .... | 434 | ............ | 100·00 | ............ | 100·00 |

Stenhouse's formula is half the above.

Scoparin puffs up when *heated*, carbonises without subliming, and burns with bright flame. — A solution in *potash* or in *acids* is decomposed by boiling, with formation of a greenish-brown resin. — Scoparin assumes a blue-green colour with *bromine*, and a dark-green with *solution of chloride of lime*. — With *nitric acid* it forms picric acid.

Scoparin is sparingly soluble in cold, more freely soluble in hot water, forming pale-yellow solutions. It dissolves slightly in strong *acids*, very easily, with deep yellowish-green colour, in caustic ammonia, the fixed alkalis and alkaline carbonates, less easily in lime- and baryta-water. The ammoniacal solution leaves, on spontaneous evaporation, a green jelly nearly free from ammonia.

Scoparin throws down greenish-yellow flocks from *neutral* and *basic acetate of lead*. It does not precipitate *corrosive sublimate* or *nitrate of silver*.

Soluble in cold, and more freely in hot *alcohol*.

*Primary Nucleus* $C^{42}H^{32}$; *Oxygen-nucleus* $C^{42}H^{30}O^2$.

## Cardol.

$$C^{42}H^{30}O^4 = C^{42}H^{30}O^2,O^2.$$
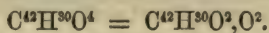
STÄDELER. *Ann. Pharm.* 63, 137; abstr. *J. pr. Chem.* 43, 250; *Pharm. Centr.* 1848, 65; *Chem. Gaz.* 1848, 29 and 58; *N. J. Pharm.* 13, 457; *Kopp's Jahresber.* 1847 and 1848, 574.

*Kardöl.* The acrid oily principle occurring, together with anacardic acid, in the pericarp of the fruit of *Anacardium occidentale* (Handbuch, viii; [2], 8).

*Preparation.* The pericarp of the nut, freed from the mild oily kernel, is bruised and exhausted with ether; the ether is distilled off; and the residue is freed from tannic acid by washing with water. The remaining mixture of about 90 p. c. anacardic acid, 10 p. c. cardol, and a little ammonia-salt, is dissolved in 15 or 20 parts of alcohol, and the solution is digested with freshly precipitated hydrated oxide of lead, so long as it remains acid, and until the whole of the anacardic acid is precipitated. The liquid is then filtered, boiled with small quantities of hydrated oxide of lead (whereby ammonia is evolved and a violet lead-compound precipitated), again filtered, and freed

from alcohol by distillation. There then remains dark wine-red cardol, a moderately strong alcoholic solution of which is to be mixed first with water till cloudiness is produced, then with aqueous neutral acetate of lead, and afterwards boiled and decolorised by dropping into it basic acetate of lead, which throws down a brown glutinous precipitate. The decolorised solution is freed from lead by sulphuric acid, and after distilling off the alcohol, the remaining cardol is washed with water.

*Properties.* Yellow oil, exhibiting a reddish tinge when in considerable quantity. Sp. gr. 0·978 at 23°. Inodorous in the cold, but has a slight agreeable odour when warmed. Neutral. It inflames and blisters the skin, producing wounds which heal very slowly.

|        |     | at 100°. |        |        |        | Städeler. |        |        |
|--------|-----|----------|--------|--------|--------|-----------|--------|--------|
| 42 C   | ... | 252      | ...... | 80·25  | ...... | 79·91     | ...... | 79·98  |
| 30 H   | ... | 30       | ...... | 9·55   | ...... | 9·86      | ...... | 9·80   |
| 4 O    | ... | 32       | ...... | 10·20  | ...... | 10·23     | ...... | 10·22  |
| $C^{42}H^{30}O^4$ | ... | 314 | ...... | 100·00 | ...... | 100·00 | ...... | 100·00 |

Städeler's formula contains 1 atom of hydrogen more, making the number of hydrogen-atoms uneven.

*Decompositions.* 1. Cardol is not volatile without decomposition; it yields by *dry distillation* a moderately limpid oil. — 2. When pure it alters but slowly in the *air*, acquiring a darker colour.— It *burns* with a bright, very smoky flame. — 3. Moderately dilute *nitric acid* converts it into a thick cochineal-red liquid, insoluble in ammonia and potash, but soluble therein on addition of alcohol, forming a solution from which neutral acetate of lead throws down violet flocks. — On dropping cardol into cooled nitric acid of sp. gr. 1·3, a brick-red mass is produced, with evolution of gas, the ultimate product being a vermilion-red powder, which dissolves with difficulty in water and alcohol, and colours the water yellow, even on repeated washing, without giving up the whole of the nitric acid. Hot nitric acid acts violently on cardol, producing an abundant evolution of nitric oxide, and converting it into an orange-red resin, which dissolves with yellow colour on boiling, and is precipitated by water or neutral acetate of lead. On evaporating the nitric acid solution to dryness, fatty acids were volatilised, and the residue, when more strongly heated, seemed to yield a sublimate of suberic acid: the cardol employed, however, was not quite pure. — 4. The deep-red solution of cardol in oil of vitriol, on absorbing moisture, deposits brown-yellow crusts, which are insoluble in water; water added to the solution throws down a little coloured gum, soluble in pure water. No conjugated compound of sulphuric acid is formed thereby. — 5. Under a layer of moderately strong *caustic potash*, cardol is converted into a tough yellow mass, which afterwards dissolves. The solution assumes a blood-red colour in the air, and forms red or violet precipitates with salts of the earths and heavy metals.

When the red alkaline solution is saturated with carbonic acid and evaporated, and the residue is digested with alcohol and filtered from carbonate of potash, a filtrate of a fine red colour is obtained, from which neutral acetate of lead throws down a little carbonate of lead. After removing this last, the addition of a little ammonia throws down a violet precipitate, soluble in pure alcohol, and precipitable again by

ammonia. The precipitate contains 68·2 p. c. oxide of lead, 27·5 p. c. C., 3·2 H., and 6·5 O. — When the alkaline solution is exposed to the air for some time at a temperature of 60° to 80°, whereby it acquires a brown-red colour, and is then saturated with carbonic acid, a solid brown resin is deposited, which may be freed from adhering carbonate of potash by washing with water. This resin dissolves in ether, also in alcohol, with the exception of a black-brown potash-compound; the solution appears red-brown by transmitted, and of a fine green colour by reflected light, and is rendered dark-yellow by acids. From the alcoholic solution neutral acetate of lead throws down a red-brown precipitate, soluble in ether and re-precipitable by alcohol. The precipitate contains, at 80°, 32·08 p. c. PbO., 50·96 C., 6·05 H., and 11·47 O., corresponding approximately with the formula $C^{84}H^{60}O^{14}, 3PbO$.

6. A mixture of cardol and hydrated oxide of lead, moistened with alcohol, and exposed to the air, assumes a violet colour, whereupon boiling alcohol extracts from it a red lead-compound, leaving the greater part of a brownish colour behind. — 7. Cardol throws down from *nitrate of silver*, on addition of ammonia, pale-yellow flocks, which decompose rapidly, with separation of silver.

Cardol is insoluble in *water*.

*Compound of Cardol with Oxide and Acetate of Lead.* — A solution of cardol in weak spirit free from air, does not precipitate neutral acetate of lead, but produces with the basic acetate, a white precipitate, which rapidly assumes a flesh-red to brown-red colour in the air, and must be washed and dried in a vacuum. Oil of vitriol decomposes it, evolving acetic acid.

|  | | *at 60°.* | | | | Städeler. |
|---|---|---|---|---|---|---|
| 46 C | 276 | ........ | 33·94 | ........ | 34·25 |
| 33 H | 33 | ........ | 4·05 | ........ | 4·20 |
| 7 O | 56 | ........ | 6·89 | ........ | 6·74 |
| 4 PbO | 448 | ........ | 55·12 | ........ | 54·81 |
| $C^4H^8PbO^4, C^{42}H^{30}O^4, 3PbO$ ........ | 813 | ........ | 100·00 | ........ | 100·00 |

Cardol dissolves easily in *alcohol* and *ether*.

### *Appendix to Cardol.*

## Anacardic Acid.

STÄDELER. *Ann. Pharm.* 63, 137.

Occurs, together with cardol (p. 517), in the pericarp of the nut of *Anacardium occidentale*.

In the preparation of cardol described at p. 517, anacardic acid is thrown down as lead-salt, together with decomposition-products of cardol. The pure lead-salt may be obtained by filtering the alcoholic solution at the proper point from the brown resin which is first thrown down, and treating the filtrate with freshly precipitated oxide of lead. But inasmuch as a large quantity of anacardic acid is carried down in the first precipitate, it is better to precipitate the alcoholic solution completely with hydrated oxide of lead, wash the precipitate with

alcohol so long as the wash-liquids are rendered cloudy by water, and decompose the lead-salt under water by hydrosulphate of ammonia. From the solution of the ammonia-salt, dilute sulphuric acid throws down the anacardic acid as a soft mass, which afterwards solidifies, and after washing with water, dissolves in alcohol, leaving sulphur and sulphide of lead. The alcoholic solution is still coloured: it must therefore be mixed with water till cloudiness is produced, then heated, and basic acetate of lead dropped into the liquid so long as colouring matter (together with a little anacardic acid) is thrown down in the form of dark oily drops. The anacardic acid may be recovered from the precipitate by dissolving it in alcohol, adding water till turbidity is produced, dropping basic acetate of lead into the liquid, and removing the coloured precipitate. — The solutions thus obtained are boiled with moist carbonate of baryta; the brown pellicle which forms is removed after 12 hours; the now colourless solution, after addition of alcohol, is precipitated at the boiling heat with alcoholic neutral acetate of lead; and the precipitate is decomposed by alcoholic sulphuric acid. After filtering from sulphate of lead, distilling off the alcohol, and adding water, the anacardic acid separates in the form of an oil, which afterwards solidifies.

*Properties.* White crystalline mass, melting at 26°, and crystallising slowly on cooling. It is inodorous in the cold, but exhales an odour at 100°, without losing weight, and does not yield condensable products at 150°. It tastes slightly aromatic, afterwards burning, but does not produce blisters. It leaves a greasy stain on paper, and when dissolved in alcohol reddens litmus strongly.

| | | *Calculation according to Städeler.* | | | Städeler. *mean.* |
|---|---|---|---|---|---|
| 44 C | 264 | ............ | 75·04 | ............ | 75·05 |
| 32 H | 32 | ............ | 9·07 | ............ | 9·18 |
| 7 O | 56 | ............ | 15·89 | ............ | 15·77 |
| C$^{44}$H$^{32}$O$^7$ | 352 | ............ | 100·00 | ............ | 100·00 |

Städeler's formula is not admissible, but no other formula is consistent with the analysis. Limpricht (*Lehrb.* 1103) doubles the formula: the acid, may, however, with greater probability be regarded as a mixture, perhaps containing fatty acids (Kr.).

*Decompositions.* 1. Anacardic acid, heated above 200°, yields a distillate of colourless limpid oil. — 2. On long exposure to the *air*, it deliquesces and turns rancid. — *Burns* with bright smoky flame. — 3. *Oil of vitriol* dissolves the acid freely, with light blood-red colour, and the solution on absorbing water deposits a tough resin, which dissolves in ammonia, and is re-reprecipitated by acids. — The acid colours cold *nitric acid* of sp. gr. 1·3 yellow, and is converted thereby into a pale-yellow elastic mass. Hot nitric acid evolves a large quantity of nitric oxide, and produces a yellow scum, which afterwards dissolves, and appears to form suberic and butyric acids.

*Combinations.* Anacardic acid forms with *bases*, partly crystalline partly amorphous salts, which emit a fatty odour at 100°, without losing weight. According to Städeler, the salts are *mono-* or *semiacid,*

*Ammonia-salt.* When the syrupy solution of anacardic acid in aqueous ammonia is evaporated in a vacuum, there remains a soap, which dissolves in water only after addition of ammonia, and is precipitated from the solution by sal-ammoniac.

*Potash-salt.* Anacardic acid, added to a moderately dilute solution of caustic potash so long as it dissolves, forms a solution which is not precipitated by water, but which deposits white flocks on passing into it a current of carbonic acid. When the solution, together with the precipitate, is evaporated to dryness in a vacuum, and the residue is exhausted with ether, the ethereal solution leaves on evaporation a white amorphous mass, easily soluble in alcohol and water, and precipitable by saline solutions. It contains 12·06 p. c. potash, and is, therefore, the mono-acid salt, $C^{44}H^{31}KO^7$ (calc. 14·22 p. c. KO.).

*Baryta-salt.* The precipitate thrown down from the ammonia-salt by chloride of barium turns brown on drying, and contains, at 80°, 31·30 p. c. of baryta (calc. for $C^{44}H^{30}Ba^2O^7$ requires 31·41 p. c. BaO.).

*Lime-salt.* Alcoholic chloride of calcium throws down from an alcoholic solution of anacardic acid, on addition of ammonia only, a granular or gelatinous precipitate, which dries up to brown particles. It contains, at 60°, 13·76 p. c., and at 100°, 13·97 p. c. lime ($C^{44}H^{30}Ca^2O^7$ requires 14·33 p. c. CaO.).

*Lead-salt.* Alcoholic neutral acetate of lead throws down from the boiling alcoholic acid, a heavy, granular, micro-crystalline precipitate, which turns yellow and rancid when kept.

|  |  |  |  |  | Städeler. mean. |
|---|---|---|---|---|---|
| 44 C | 264 | ........ | 47·43 | ........ | 47·23 |
| 30 H | 30 | ........ | 5·37 | ........ | 5·43 |
| 5 O | 40 | ........ | 7·18 | ........ | 6·92 |
| 2 PbO | 224 | ........ | 40·02 | ........ | 40·42 |
| $C^{44}H^{30}Pb^2O^7$ | 558 | ........ | 100·00 | ........ | 100·00 |

*Compound of the Lead-salt with Acetate of Lead.* — This body was obtained on one occasion, in winter, as follows: The ethereal solution of anacardic acid and cardol obtained by exhausting the pericarp, was evaporated; the residue dissolved in alcohol; and the solution was mixed with water till cloudiness was produced, and precipitated with alcoholic neutral acetate of lead, so that the greater part of the anacardic acid was thrown down, together with colouring matter, in the form of a brown resin. This precipitate, washed with alcohol and dissolved in warm alcohol containing acetic acid, yielded a brown turbid liquid, from which, after the separation of the deposit, the double salt crystallised in the cold. It forms white, pearly laminæ, resembling cholesterin, permanent in the air, and feeling like talc. With oil of vitriol it evolves acetic acid. When heated, it puffs up to a white froth, evolving a large quantity of acetic acid, and afterwards melts to a colourless oil, turns brown, and decomposes. — In warm water it becomes viscid without dissolving. It is insoluble in cold alcohol, and decomposes when boiled therewith, with separation of the lead-salt of anacardic acid. Ether extracts from the compound the lead-salt of anacardic acid, leaving the acetate undissolved.

|  |  | at 50°. |  |  |  | Städeler. |
|---|---|---|---|---|---|---|
| 48 C | ................................... | 288 | ........ | 46·71 | ........ | 47·07 |
| 34 H | ................................ | 34 | ........ | 5·50 | ........ | 5·55 |
| 9 O | ................................... | 72 | ........ | 11·66 | ........ | 10·94 |
| 2 PbO | ................................ | 224 | ........ | 36·13 | ........ | 36·44 |
| $C^{44}H^{31}PbO^7 + C^4H^3PbO^4$ | .... | 618 | ........ | 100·00 | ........ | 100·00 |

The ammonia-salt precipitates *cobalt salts* violet, *nickel salts* white, and *ferrous sulphate* white.

*Ferric salt.* — A mixture of alcoholic anacardic acid and alcoholic sesquichloride of iron, throws down, on addition of ammonia (not sufficient to neutralise the acid), a dark-brown resinous precipitate, containing, at 60°, 18 p. c. sesquioxide of iron.

*Silver-salt.* — Alcoholic nitrate of silver throws down from strong alcoholic solutions of anacardic acid, a white precipitate, which blackens slowly and slightly in the air, excepting when an excess of ammonia is also added. The salt decomposes at 130°, melting to a fine steel-blue mass. It dissolves in alcohol, especially when acidulated.

|  |  | at 80°. |  |  |  | Städeler. |
|---|---|---|---|---|---|---|
| 44 C | ................... | 264 | ........ | 57·56 | ........ | 57·56 |
| 31 H | ................ | 31 | ........ | 6·74 | ........ | 6·82 |
| 6 O | ................... | 48 | ........ | 10·45 | ........ | 10·25 |
| AgO | ............. | 116 | ........ | 25·25 | ........ | 25·37 |
| $C^{44}H^{31}AgO^7$ | .... | 459 | ........ | 100·00 | ........ | 100·00 |

Anacardic acid dissolves easily in *alcohol* and *ether*. It is not converted into an ether by passing hydrochloric acid gas into its alcoholic solution.

### Oxygen-nucleus  C⁴²H²⁸O⁴.

# Helenin.

$$C^{42}H^{28}O^6 = C^{42}H^{28}O^4,O^2\;?$$
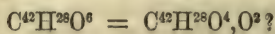
GEOFFROY. *Traité de la matière medicale*, 6, 247.
NEUMANN. *Chemie*, Dresden, 1755, 1, 746.
DEHNE. *Crell. Chem. J.* 3, 12.
HOFFMANN. *Taschenbuch*, 1787, 150.
KRÜGER & CORVINUS. *Scher. J.* 7, 575.
FUNKE. *A. Tr.* 18, 1, 74; *Ann. Chim.* 76, 102.
JOHN. *Chem. Schriften*, 4, 64.
FR. NEES V. ESENBECK. *Br. Arch.* 28, 3.
GERHARDT. *Ann. Chim. Phys.* 72, 163; *Ann. Pharm.* 34, 192; abstr. *J. pr. Chem.* 20, 47. — *N. Ann. Chim. Phys.* 12, 188; *Rev. scient.* 19, 15; *J. pr. Chem.* 35, 66; abstr. *Berz. Jahresber.* 25, 659.

*Alantcampher.*

Noticed by Lefébure and by Geoffroy & Spiess; described more exactly by Hoffmann and by Krüger & Corvinus; and completely investigated by Gerhardt.

*Source.* In the root of *Inula Helenium.* Crystallises, contaminated with resin, from *Tinctura Helenii* (Krüger & Corvinus); crystallises or sublimes frequently from the alcoholic extract. See Rump (*N. Br. Arch.* 32, 215), H. Müller (*N. Br. Arch.* 32, 216), Groneweg (*N. Br. Arch.* 37, 266). — Röttscher (*N. Br. Arch.* 30, 169) regarded such crystals as benzoic acid. — Elecampane-root 5 or 6 years old, when dried in an oven, yielded a sublimate of helenin, which was not obtained from the fresh root (Rich, *N. J. Pharm.* 5, 74).

Fine white needles, melting at 75°, which crystallised, after long standing, from *Extractum Inulæ spirituosum* prepared from old root, contained 64·01 p. c. C., 9·27 H., and 26·72 O., corresponding with the formula $C^{16}H^{14}O^5$, and not agreeing with Gerhardt's analysis of helenin (Hoyer, *Pharm. Viertelj.* 13, 554).

*Preparation.* 1. The fresh root, sliced, is boiled with alcohol of 80 p. c.; and the hot filtrate is mixed with 3 or 4 times its volume of cold water, whereupon it becomes slightly turbid, and in the course of 24 hours deposits the helenin in white needles (Delffs, *Pogg.* 80, 440). Gerhardt exhausts the fresh root with alcohol of 36°, distils off the greater part of the alcohol, and cools the liquid, whereupon the helenin crystallises. It is purified by several times repeated crystallisation from alcohol. — The tincture of the dried root yields on evaporation a brown oily layer, which is difficult to purify, and solidifies on cooling (Gerhardt). — 2. When the root is distilled with 5 parts of water, the helenin passes over as an oil, partly solidifying at the bottom of the distillate, and partly crystallising from the liquid in needles (Funke; John). The distillate deposits brown flocks, which yield helenin when dissolved in alcohol and evaporated, whilst an oil remains in solution (Nesenbeck). In this way helenin is obtained pure, but in too small quantity (Gerhardt).

*Properties.* White, four-sided, brittle prisms (Gerhardt). According to Gerhardt, it is lighter, according to others, heavier than water. It has a very faint odour and taste (Gerhardt); according to older statements it has the odour of elecampane, and has a peculiar aromatic taste. Its vapour produces stupefaction (John). It melts to an oil at 72°, and solidifies to a crystalline mass on cooling, but not after being kept in the melted state for a few minutes (Gerhardt). It sublimes undecomposed in talc-like laminæ, and distils with vapour of water. According to Gerhardt, it boils at 275° to 280°, evolving a very faint odour, and undergoing partial decomposition. Neutral.

| | | | | Dumas. | | Gerhardt. mean. | | |
|---|---|---|---|---|---|---|---|---|
| | | | | (*J. pr. Chem.* 4, 434) | | Earlier. | | Later. |
| 42 C | ............... | 252 | ........ | 76·83 | ........ | 76·9 | ........ | 77·15 | ........ | 76·46 |
| 28 H | ............... | 28 | ........ | 8·53 | ........ | 8·8 | ........ | 8·54 | ........ | 8·66 |
| 6 O | ............... | 48 | ........ | 14·64 | ........ | 14·3 | ........ | 14·31 | ........ | 14·88 |
| $C^{42}H^{28}O^6$ | ........ | 328 | ........ | 100·00 | ........ | 100·0 | ........ | 100·00 | ........ | 100·00 |

Gerhardt's earlier formula was $C^{30}H^{20}O^4$. According to Dumas, $C^{14}H^9O^2$.

*Decompositions.* 1. Helenin dissolves in moderately dilute *nitric acid*, and is precipitated from the solution by water in its original state. Fuming or hot dilute nitric acid evolves a large quantity of nitric oxide and converts it into a red resin, nitrohelenin. On one occasion fine crystals, differing from oxalic acid, were obtained. — 2. Helenin dissolves in

*oil of vitriol*, forming a red solution, from which it is precipitated by water, unchanged at first: on standing, or when warmed, the solution blackens, and evolves sulphurous acid, and on addition of water throws down dirty-brown flocks. A solution of helenin in fuming sulphuric acid deposits yellow resinous flocks on addition of water, whilst free sulphuric acid and helenin-sulphuric acid remain in solution. The easily soluble bitter baryta-salt of the latter acid decomposes when the solution is evaporated at a gentle heat. Helenin does not yield an oil when distilled with oil of vitriol. — 3. By distillation with anhydrous *phosphoric acid* it yields helenene (p. 13). — 4. Helenin is not acted upon by dry *chlorine* at ordinary temperatures, even in sunshine ; but on passing chlorine over fused helenin, chlorhelenin and hydrochloric acid are formed. — 5. Helenin absorbs *hydrochloric acid* gas, assuming a yellow colour. It is coloured dark-red by *stannic chloride* and *ter-chloride of antimony*. — 6. It is not decomposed by heating with aqueous or alcoholic *potash :* when heated with the fused hydrate, the greater part is volatilised, and a portion is carbonised. On heating it to 250° with *potash-lime*, it evolves hydrogen abundantly ; the residue dissolved in water, deposits, on addition of hydrochloric acid, a large quantity of sticky resinous flocks. Helenin distilled with caustic *lime*, yields a yellow oil having an odour of acetone (Gerhardt).

Helenin is insoluble in *water* (Nesenbeck ; Gerhardt). It is nearly insoluble in cold, and very slightly soluble in boiling water (Krüger & Corvinus). It absorbs hydrochloric acid gas, and dissolves in oil of vitriol and in nitric acid (see above). It absorbs sulphurous acid, forming a liquid which under diminished pressure gives off the gas and again becomes crystalline (Bineau, *N. Ann. Chim. Phys.* 24, 335).

Helenin dissolves in hot strong *caustic potash* and is precipitated undecomposed by acids (Gerhardt). — It dissolves in strong *acetic acid*, forming a colourless solution, which when evaporated or mixed with water, deposits crystals of helenin (Gerhardt). — It dissolves with difficulty in cold, and easily in hot *alcohol*, from which it crystallises on evaporation, and is precipitated in flocks by water (Krüger & Corvinus). — It is easily soluble in *ether*, *oil of turpentine* (John), *volatile* and *fatty oils*, and *creosote* (Gerhardt ; Nesenbeck).


# Nitrohelenin.

GERHARDT. *Ann. Chim. Phys.* 72, 172.

Helenin is warmed with an excess of moderately strong nitric acid till the product formed is soluble in ammonia ; the ammoniacal solution is dropped into water ; and the yellow precipitate is purified by dissolving it in alcohol and precipitating with water.

Yellow friable mass containing nitrogen and, on the average, 55·38 p. c. C., 5·98 H., besides oxygen. Gerhardt formerly proposed the formula $C^{30}X^2H^{18}O^4$.

Nitrohelenin is not volatile without decomposition. — It is converted into oxalic acid by an excess of nitric acid. — With melted hydrate of potash it evolves ammonia.

Slightly soluble in *water ;* easily soluble in *nitric acid.* Dissolves very easily in aqueous *ammonia* with red colour, and is precipitated from

the solution as a rust-brown powder by acids, also by salts of lead and silver. — Dissolves easily in *alcohol.*

# Chlorhelenin.

$$? \, C^{42}Cl^4H^{24}O^6 \; = \; C^{42}Cl^4H^{24}O^4,O^2.$$

GERHARDT. *Ann. Chim. Phys.* 72, 175. — *N. Ann. Chim. Phys.* 12, 189.

*Chlorhydrate de Chlorhellenine.*

*Formation.* See p. 524.

*Preparation.* Dry chlorine is passed over helenin fused in a water-bath so long as the mass continues to give off vapours of hydrochloric acid, and the residue is boiled with alcohol. The yellow flocks deposited from the yellow tincture on cooling, are washed and dried in a vacuum at 100°.

Yellow powder, lighter than water.

|  |  |  |  |  |  |  | Gerhardt. mean. |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | *a.* |  | *b.* |  |  | *c.* |
| 42 C | 252 | ........ | 54·08 | ........ | 47·39 | ........ | 52·3 | ........ | 52·5 |
| 24 H | 24 | ........ | 5·15 | ........ | 5·51 | ........ | 5·7 | ........ | 5·7 |
| 4 Cl | 142 | ........ | 30·47 | ........ | 37·10 | ........ | 30·6 | ........ | 30·2 |
| 6 O | 48 | ........ | 10·30 | ........ | 10·00 | ........ | 11·4 | ........ | 11·6 |
| $C^{42}H^{24}Cl^4O^6$ | 466 | ........ | 100·00 | ........ | 100·00 | ........ | 100·0 | ........ | 100·0 |

*a, b,* and *c* were different preparations. Gerhardt himself considers the formula doubtful (*Traité* 4, 297).

Chlorhelenin *heated* below its melting-point gives off a large quantity of hydrochloric acid gas, leaving a chlorinated resin, which carbonises when more strongly heated. — It *burns* with difficulty, with a green-edged flame. — Produces with *oil of vitriol* a fine carmine-red coloration, which disappears on addition of water. — Dissolves easily in hot *caustic potash,* with formation of chloride of potassium and a yellowish-red solution, from which hydrochloric acid throws down red chlorinated flocks. — Chlorhelenin passed over red-hot *quick-lime* yields naphthalin, leaving a large quantity of carbon.

Chlorhelenin is insoluble in *water.* It dissolves slightly in cold, and more easily in hot *alcohol,* forming a yellow solution from which it is precipitated in light flocks by water. — It dissolves very easily in *ether.*

*Oxygen-nucleus* $C^{42}H^{22}O^{10}$.

# Philygenin.

$$C^{42}H^{24}O^{12} \; = \; C^{42}H^{22}O^{10},H^2O^2.$$
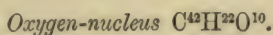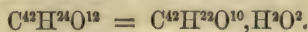
BERTAGNINI. *Ann. Pharm.* 92, 109.
BERTAGNINI & LUCA. *Compt. rend.* 51, 368.

Formed, together with grape-sugar, by boiling philyrin with dilute hydrochloric acid, and deposited from the liquid in resinous drops.

White pearly crystalline mass, fusible without decomposition or loss of weight.

| | Crystals. | | | Bertagnini. | | Bertagnini. & Luca. |
|---|---|---|---|---|---|---|
| 42 C ............... | 252 | ........ | 67·74 | ........ | 67·71 | ........ 67·67 |
| 24 H ............... | 24 | ........ | 6·45 | ........ | 6·67 | ........ 6·46 |
| 12 O ............... | 96 | ........ | 25·81 | ........ | 25·62 | ........ 25·87 |
| $C^{42}H^{24}O^{12}$ ........ | 372 | ........ | 100·00 | ........ | 100·00 | ........ 100·00 |

Polymeric with saligenin (xii. 233).

Philygenin is violently attacked by *nitric acid,* and is coloured amaranth-red by *oil of vitriol.* It is not acted upon by dilute acids or by an alkaline solution 'of cupric oxide. — With *chlorine, bromine,* and *nitric acid,* it forms the following products :—

Bibromophilygenin   $C^{42}Br^2H^{22}O^{12}$;   Bichlorophilygenin   $C^{42}Cl^2H^{22}O^{12}$;
Nitrophilygenin   $C^{42}XH^{23}O^{12}$;   Binitrophilygenin   $C^{42}X^2H^{22}O^{12}$;
Bromonitrophilygenin $C^{42}BrXH^{22}O^{12}$;   Chloronitrophilygenin $C^{42}ClXH^{22}O^{12}$.

Philygenin is nearly insoluble in cold, and but slightly soluble in boiling *water.* — It dissolves in *potash* and *ammonia;* less freely than philyrin in *alcohol;* easily in *ether,* from which it crystallises.

*Glucoside of Philygenin.*

## Philyrin.

$$C^{54}H^{34}O^{22} = C^{42}H^{24}O^{12}, C^{12}H^{10}O^{10}.$$
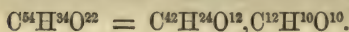
CARBONCINI. *Gaz. eclettica di chimica. November* 1836. *Repert.* 58, 323; *Ann. Pharm.* 24, 242; *Berz. Jahresber.* 17, 306.

C. BERTAGNINI. *Ann. Pharm.* 92, 109; *Pharm. Centr.* 1855, 124; *Pharm. Viertelj.* 4, 436; *N. Phil. Mag.* 9, 78; *N. Ann. Chim. Phys.* 43, 351.

BERTAGNINI & LUCA. *Compt. rend.* 51, 368; abstr. *Ch. Pharm. Zeitschr.* 3, 779; *Chem. Centr.* 1861, 29.

*Phillyrin,* more properly philyrin, from φίλυρα (Wittstein, *Pharm. Viertelj.* 4, 436).

*Source.* In the stone-linden tree, *Philyrea latifolia* and *media,* most abundant in the bark, in smaller quantity in the leaves.

*Preparation.* A decoction of the coarsely powdered bark is evaporated down to four times the weight of the bark employed; it is then clarified by means of albumin, and, after cooling, mixed with milk of lime to slightly alkaline reaction, and left at rest for 20 or 30 days. The deposit formed is collected, dried, powdered, and exhausted with boiling alcohol of 55°; and the tincture thus obtained is digested with animal charcoal, filtered, freed from alcohol by distillation, mixed with water, and set aside to crystallise (Carboncini). Bertagnini treats the

decoction of the bark with oxide of lead or lime, and evaporates the filtrate, from which the philyrin crystallises.

The crystals lose their water (see below) over oil of vitriol, or when warmed, and the anhydrous philyrin afterwards melts at 160° to a colourless liquid, which solidifies to a fissured mass on cooling.— Inodorous; very slightly bitter (Bertagnini). According to Carboncini it is tasteless in itself at first, but afterwards, or when dissolved, very bitter and acrid.

| | *Anhydrous.* | | | | Bertagnini & de Luca. *mean.* |
|---|---|---|---|---|---|
| 54 C | 324 | ......... | 60·67 | ......... | 60·53 |
| 34 H | 34 | ......... | 6·37 | ......... | 6·37 |
| 22 O | 176 | ......... | 32·96 | ......... | 33·10 |
| $C^{54}H^{34}O^{22}$ .... | 534 | ......... | 100·00 | ......... | 100·00 |

*Decompositions.* 1. Fused philyrin, *heated* to 200°, assumes a faint red colour, afterwards turning darker; at 250° it evolves empyreumatic vapours and combustible gas, and at 280° leaves charcoal.— 2. It dissolves in *oil of vitriol* with reddish-violet colour, undergoing decomposition. — 3. When boiled with dilute *hydrochloric acid*, it is broken up into philygenin and grape-sugar :

$$C^{54}H^{34}O^{22} + 2HO = C^{42}H^{24}O^{12} + C^{12}H^{12}O^{12}.$$
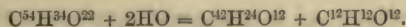
This decomposition is not effected by emulsin or by wine-yeast, but when submitted to the lactic fermentation, philyrin likewise yields philygenin and the decomposition-products of sugar. — 4. *Bromine, chlorine,* and *nitric acid* form derivatives corresponding to those of philygenin (p. 526). Bromophilyrin and chlorophilyrin crystallise in needles, and are resolved by dilute acids into bromophilygenin or chlorophilygenin and sugar. — Dilute *nitric acid* forms yellow silky crystals; stronger acid produces crystalline granules; the boiling concentrated acid forms oxalic acid and shining laminæ, with evolution of carbonic and nitrous acids.— 5. Philyrin is not acted on by an *alkaline solution of cupric oxide* (Bertagnini).

*Combinations.* — *Hydrated Philyrin.* — Philyrin crystallises from its solutions in white, very light, silvery scales, containing varying proportions of water of crystallisation, which it gives up over oil of vitriol, or when heated to 50° or 60° (Bertagnini & de Luca). Bertagnini formerly stated the proportion of water at 4·7 p. c. (3 at. = 4·8 p. c.).

| | *Crystals.* | | | | Bertagnini. *mean.* |
|---|---|---|---|---|---|
| 54 C | 324 | ........ | 57·75 | ........ | 57·77 |
| 37 H | 37 | ........ | 6·60 | ........ | 6·73 |
| 25 O | 200 | ........ | 35·65 | ........ | 35·50 |
| $C^{54}H^{34}O^{22} + 3aq.$ .... | 561 | ........ | 100·00 | ........ | 100·00 |

Philyrin dissolves in 1,300 parts of water at 9°, and freely in boiling water (Bertagnini & de Luca). It is insoluble in cold dilute acids, but soluble in warm *acetic acid*, from which it crystallises unchanged on cooling (Carboncini). It is not acted on by aqueous *ammonia* or by *alkalis*, and is not precipitated by *metallic salts* (Bertagnini).

It dissolves in 40 parts of *alcohol* at 9°, and more easily in the

hot liquid; insoluble in *ether* (Bertagnini), and in *volatile* and *fat oils* (Carboncini).

<p style="text-align:center"><em>Primary Nucleus</em> C⁴²H³⁴; <em>Oxygen-nucleus</em> C⁴²H²²O¹².</p>

# Columbin.

$$C^{42}H^{22}O^{14} = C^{42}H^{22}O^{12}, O^{2}.$$
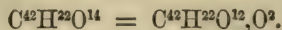
WITTSTOCK.  *Pogg.* 19, 298; *Berz. Jahresber.* 11, 288.
BUCHNER.  *Repert.* 37, 418.
LEBOURDAIS.  *N. Ann. Chim. Phys.* 24, 63; *Ann. Pharm.* 67, 251; *J. pr. Chem.* 45, 363.
BÖDEKER.  *Ann. Pharm.* 69, 47; abstr. *Pharm. Centr.* 1849, 145; *Chem. Gaz.* 1849, 149; *Kopp's Jahresber.* 1849, 477.

The bitter constituent of columbo-root from *Menispermum palmatum.* Discovered by Wittstock, Planche (*Bull. Pharm.* 3, 289) having previously described a bitter extract under the name of columbo bitter. It occurs in crystals in the cells of the root (Bödeker).

*Preparation.* The root is exhausted with alcohol of 75 p. c.; the alcohol is distilled off; and the residue evaporated to dryness over a water-bath. The dry residue is again taken up by water, and the thick turbid solution thereby formed is shaken with ether so long as that liquid takes up columbin. The ethereal layer, when decanted and freed from most of the ether by distillation, deposits the greater part of the columbin in crystals as it cools; the remainder crystallises from the oily mother-liquor on standing. The crystals are purified by washing them with cold ether, pressing, and recrystallising from boiling absolute ether, till the whole of the fat is removed, which is known by the complete solubility of the columbin in boiling acetic acid (Bödeker). Wittstock either exhausts the root with ether, leaves the solution to evaporate in the air, and purifies the crystals by dissolving them in acetic acid; or he evaporates to one-third an extract of the root with alcohol of sp. gr. 0·835, whereupon the columbin crystallises, but in a less pure state. — 16 ounces of the root yield 1 dram of columbin (Wittstock).

Lebourdais exhausts the powdered root with cold water, and allows the infusion to percolate through purified animal charcoal, which takes up columbin and colouring matter. The charcoal, after washing with cold water and drying, is exhausted with hot alcohol, which takes up the columbin and leaves it in coloured crystals on evaporation. Prolonged washing of the charcoal with water removes most of the bitter, the rest remaining in the charcoal together with nearly the whole of the colouring matter. When the aqueous solution is strained through fresh charcoal, it again gives up the whole of the columbin, which may be extracted from the charcoal, after drying, by hot alcohol, and obtained in a pure state by evaporating the solution.

*Properties.* White or translucent prisms, and slender needles, belonging to the right prismatic system. The crystals are similar to fig. 55, but with the addition of the face *m* of fig. 53. Between *m* and *u* there are faces of a second prism, too narrow to be measured. Angle *u* : *u*

$= 125° \ 30'$ ; $u : i = 152° \ 45'$ ; $u : m = 117° \ 15'$ ; $i : i' = 167° \ 19'$ ;
$i : l = 123° \ 39\frac{1}{2}'$ ; $i : u = 119° \ 31'$. The faces of the crystals are smooth
and shining. There seems to be no cleavage-plane (G. Rose, *Pogg.* 19,
441). Inodorous. Tastes very bitter. Neutral. Melts like wax
when warmed (Wittstock).

|  |  | at. 115° |  | Liebig. (*Pogg.* 21, 30). |  | Bödeker. *mean.* |
|---|---|---|---|---|---|---|
| 42 C | ............... | 252 | 65·28 | ........ 65·45 | ........ | 65·20 |
| 22 H | ............... | 22 | 5·69 | ........ 6·17 | ........ | 5·98 |
| 14 O | ............... | 112 | 29·03 | ........ 28·38 | ........ | 28·82 |
| $C^{42}H^{22}O^{14}$ | .... | 386 | 100·00 | ........ 100·00 | ........ | 100·00 |

*Decompositions.* Columbin decomposes when heated, and *burns* with
a smoky flame. — *Oil of vitriol* colours it orange, afterwards dark-red ;
water throws down from the solution a rust-coloured precipitate. —
Columbin is dissolved by nitric acid of sp. gr. 1·25 only when warmed,
with evolution of red vapours, and is partially precipitated from the
solution by water (Wittstock). — By fusion with *caustic potash* it yields
a compound from which acids throw down brown flocks. — It is not
decomposed by *emulsin* (Bödeker).

Columbin dissolves in aqueous *alkalis*, and is precipitable from the
solution by acids. — It is not precipitated from its solution in alcohol
or acetic acid by *neutral acetate of lead, nitrate of silver*, or other
metallic salts (Wittstock).

Columbin dissolves in *acetic acid* of sp. gr. 1·04 as easily as in
boiling alcohol, and crystallises from the solution in regular forms. — It
dissolves in 30 or 40 parts of boiling *alcohol* of sp. gr. 0·835, and very
slightly in cold alcohol and *ether*, though the solutions taste very bitter.
It is soluble to a slight extent in *volatile oils.* — It is not precipitated
from the solution in alcohol or acetic acid by *tincture of galls*
(Wittstock).


*Appendix to Columbin.*


## Columbic Acid.


BÖDEKER. *Ann. Pharm.* 69, 47.

Occurs, together with berberine (p. 185) and columbin, in columbo root.

The alcoholic extract of the root is dried and exhausted with hot
lime-water, and the filtrate is mixed with hydrochloric acid, not in
excess, whereby a yellow amorphous precipitate is produced. Or the
turbid aqueous solution of the alcoholic extract is mixed with a little
hydrochloric acid, and the amorphous precipitate thereby thrown down
is removed by filtration, before it becomes mixed with berberine-salt.
The precipitate is freed from admixed berberine by washing with water,
and from columbin by boiling with ether, which dissolves also a little
columbic acid, and the remainder is dissolved in caustic potash and
treated with a current of carbonic acid, which throws down a small
quantity of brown flocks. The filtrate, supersaturated with hydro-
chloric acid, deposits the columbic acid in white flocks which condense
to a pale straw-yellow powder when washed with water.

Amorphous powder, remaining in the form of a varnish on evaporating its solutions. Reddens litmus strongly. Less bitter than columbin.

The acid dried at 40° loses 2·52 p. c. of water at 100°, and as much more at 115°, corresponding altogether to 2 atoms (calc. 4·53 p. c. HO).

|  |  | at 115° |  |  |  | Bödeker. |
|---|---|---|---|---|---|---|
| 42 C | ............................ | 252 | ........ | 66·49 | ........ | 66·64 |
| 23 H | ........................ | 23 | ........ | 6·07 | ........ | 6·29 |
| 13 O | ......................... | 104 | ........ | 27·44 | ........ | 27·07 |
| $C^{42}H^{22}O^{12}$ + aq.? | .... | 379 | ........ | 100·00 | ........ | 100·00 |

Bödeker supposes the acid still to contain water.

Columbic acid *burns* with flame on platinum foil. — It is not decomposed by cold *nitric acid*. It dissolves in warm *oil of vitriol*, and is precipitated from the solution by water.

The acid is nearly insoluble in *water*, but dissolves in dilute caustic potash with pale brownish-yellow colour. — Alcoholic *neutral acetate of lead* throws down from the alcoholic solution a yellow lead-salt, which contains 30·19 p. c. of oxide of lead at 100°, but loses 4·29 p. c. of water more at 130°.

Columbic acid dissolves in *alcohol* with pale-yellow colour, very slightly in cold *ether*, and more freely in *acetic acid*.


*Primary Nucleus* $C^{42}H^{36}$; *Oxygen-nucleus* $C^{42}H^{18}O^{18}$.


### Euxanthic Acid.

$$C^{42}H^{18}O^{22} = C^{42}H^{18}O^{18},O^4.$$
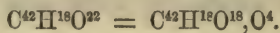
J. STENHOUSE (1844). *Phil. Mag.* 25, 322; *Ann. Pharm.* 51, 423.
O. L. ERDMANN. *J. pr. Chem.* 33, 190; 37, 386; abstr. *N. J. Pharm.* 10, 154. — *J. pr. Chem.* 71, 195.
LAURENT. *Compt. chim.* 1849, 377; abstr. *Compt. rend.* 26, 33; *Kopp's Jahresber.* 1849, 456.

*Purreesäure. Purreic acid. Acide euxanthique ou purreïque.*

Discovered simultaneously by Stenhouse and by Erdmann, and more fully examined by the latter chemist.

*Source.* In purree (*Indian yellow, Camel's urine*), a colouring matter of doubtful origin, imported from India and China, in which it occurs as magnesia-salt, amounting to about 50 per cent. of the purree (Stenhouse). On the origin of purree, see Guibourt (*Rev. scient.* 14, 18, and 23), Batka (*J. pr. Chem.* 33, 248), and Stenhouse and Erdmann (*loc. cit.*). It occurs in commerce in two varieties, crude purree and *Jaune Indien purifié*, the latter of which appears to be obtained by boiling the crude purree with water, and mixing the residue with carbonate of magnesia (Erdmann).

*Preparation.* Purree is boiled with water so long as it gives up

colouring matter, and the residue is decomposed by heating it with dilute hydrochloric acid, whereby a clear solution is obtained, which deposits euxanthic acid on cooling. The aqueous decoction contains chloride of potassium and a black pitchy substance having an excrementitious odour (on one occasion this last body was replaced by benzoate of potash), together with small quantities of euxanthate of magnesia. The mother-liquor, filtered from the acid which is deposited, yields, when evaporated, a little euxanthic acid, but contaminated with euxanthone. The acid is washed with cold water and recrystallised from alcohol, to remove magnesia and adhering organic substances, and is then converted into pure crystallised ammonia-salt, the boiling solution of which is decomposed by hydrochloric acid, whereupon the euxanthic acid is deposited on cooling, and must be recrystallised from alcohol (Erdmann). Stenhouse boils purree, cut in small pieces, with water containing a large quantity of acetic acid; filters from dark brown flocks and other impurities; adds to the filtrate neutral acetate of lead so long as a brownish-yellow bulky precipitate is thrown down; washes the precipitate with cold water; and decomposes it with hydrosulphuric acid; then boils the mass with alcohol, and filters from sulphide of lead. On cooling the alcoholic solution, euxanthic acid crystallises, but as it still contains a large quantity of magnesia, it is dissolved in a hot solution of carbonate of soda; the solution is filtered; the filtrate is decomposed by hydrochloric acid; the euxanthic acid thereby thrown down is washed with cold water, pressed, dissolved in hot water, and again precipitated with neutral acetate of lead; and the precipitate decomposed by hydrosulphuric acid, and boiled out with alcohol. The acid which crystallises from the alcoholic solution is, lastly, purified by recrystallising it five or six times from alcohol.

Euxanthic acid thus obtained contains 2 atoms of water, which may be expelled by heating to 130°.

*Properties.* See Hydrated Euxanthic acid (p. 532).

|  |  |  | Stenhouse. *mean* at 130°. | | Erdmann. *mean* at 130°. | | Laurent. |
|---|---|---|---|---|---|---|---|
| 42 C .............. | 252 | ........ | 56·50 | ........ | 55·08 | ........ 56·35 | ........ 56·37 |
| 18 H .............. | 18 | ........ | 4·04 | ........ | 4·43 | ........ 4·03 | ........ 4·07 |
| 22 O .............. | 176 | ........ | 39·46 | ........ | 40·49 | ........ 39·62 | ........ 39·56 |
| $C^{42}H^{18}O^{22}$ ........ | 446 | ........ | 100·00 | ........ | 100·00 | ........ 100·00 | ........ 100·00 |

Erdmann proposed the formula $C^{40}H^{16}O^{21}$; Stenhouse, $C^{20}H^{9}O^{11}$; Gerhardt, (*N. J. Pharm.* 10, 157) the one above given, which was confirmed by Laurent's experiments (*Compt. Chim.* 1849, 377), and was afterwards adopted by Erdmann himself (*J. pr. Chem.* 71, 195). — The formation of hamathionic acid, together with euxanthone, by the action of oil of vitriol on euxanthic acid, and likewise the formation of terchloreuxanthone, $C^{40}Cl^{3}H^{9}O^{12}$, on dissolving bichloreuxanthic acid in oil of vitriol, throw doubt, if not upon the empirical correctness of this formula, at least upon the relation between euxanthone (p. 181) and euxanthic acid which it seems to express (Kr.).

*Decompositions.* 1. Euxanthic acid *burns* with bright flame on platinum foil (Erdmann). — 2. It melts when *heated* to 160° or 180°, evolving carbonic acid and water, and is converted into euxanthone, which sublimes at a stronger heat (Erdmann; Stenhouse). In this reaction no other product than carbonic acid and water is evolved:

$$C^{42}H^{18}O^{22} = C^{40}H^{12}O^{12} + 2CO^2 + 6HO \text{ (Laurent).}$$
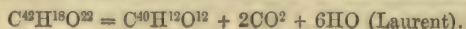
In a sublimation apparatus the acid partially carbonises, and yields an abundant sublimate of euxanthone (Stenhouse). — 3. It dissolves freely in *oil of vitriol*, becoming hot, and forming a yellow or reddish-yellow solution, without evolution of gas; after some time the solution solidifies to a pulpy mass of euxanthone, whilst hamathionic acid remains in solution (Erdmann). The filtrate reduces alkaline solutions of cupric oxide (W. Schmid, *Ann. Pharm.* 93, 88).

On diluting the solution in sulphuric acid with water, separating the precipitated euxanthone, and saturating the filtrate with carbonate of baryta, a yellow liquid containing baryta is obtained, which when evaporated deposits brown flocks and turns acid. When evaporated in a vacuum, it leaves Erdmann's *hamathionate of baryta* in the form of a brown gum containing 31·43 p. c. of baryta, from a solution of which basic acetate of lead throws down a yellow amorphous lead-salt containing 13·89 p. c. C., 1·16 H., 15·75 O., 6·82 $SO^3$, and 62·38 PbO. The aqueous hamathionic acid, separated from the lead-salt by hydrosulphuric acid, forms a very acid syrup (Erdmann).

4. Euxanthic acid is converted by *bromine* into bromeuxanthic acid, and by aqueous *chlorine* into chloreuxanthic acid. Excess of chlorine converts it into a yellow powder, the brown solution of which in caustic ammonia or its carbonate, does not yield crystals (Erdmann). — 5. Alcoholic euxanthic acid is converted into euxanthone on passing hydrochloric acid gas into it (Erdmann).

6. Cold *nitric acid* of sp. gr. 1·31 converts euxanthic acid, on standing for 24 hours, into nitroeuxanthic acid without dissolving it. Traces of oxalic acid are also formed. When euxanthic acid is heated with nitric acid, a violent evolution of gas takes place, and a dark reddish-yellow solution is formed, which deposits coccinonic acid on cooling, and contains also oxalic acid. By prolonged boiling, styphnic acid is produced, but ultimately the liquid contains only oxalic acid Erdmann). See xi, 230. Purree heated with pure nitric acid yields stychnic acid, and with nitric acid containing hydrochloric acid a large quantity of oxalic acid (E. Kopp, *Compt. chim.* 1849, 153).

Erdmann's *coccinonic acid* forms yellow crystalline granules, containing 38·6 to 44·5 p. c. C., and 1·09 to 2·07 H.; its scarlet potash-salt contains 19·42 p. c. of potash. Probably a mixture of various nitro-acids.

7. Euxanthic acid is decomposed by boiling with *oxide of manganese* and *sulphuric acid*, with formation of formic acid (Stenhouse). — 8. It dissolves in melted *hydrate of potash*, with scarlet colour, and is precipitated by acids in the form of a resin (Stenhouse). — 9. The acid does not reduce *alkaline solutions of cupric oxide* (W. Schmid, *Ann. Pharm.* 93, 88).

*Combinations. — With Water.* — A. *Hydrated Euxanthic acid.*

a. *With* 2 *at. Water.* — Crystallises from alcohol in pale straw-yellow, shining needles, which give off 4·35 p. c. of water at 130° (Erdmann). Tastes sweetish at first, and afterwards slightly bitter.

|  | Crystals. |  |  | Erdmann. |
|---|---|---|---|---|
| $C^{42}H^{18}O^{22}$ .................... | 446 | ........ | 96·13 | |
| 2 HO .................... | 18 | ........ | 3·87 | ........ 4·35 |
| $C^{42}H^{18}O^{22}$ + 2aq. .... | 464 | ........ | 100·00 | |

b. *With 6 at. Water.* — The euxanthic acid precipitated from the ammonia-salt by hydrochloric acid loses 10·98 p. c. of water on drying (Erdmann).

Erdmann.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C^{42}H^{18}O^{22}$ | ................ | 446 | ........ | 89·2 | | |
| 6 HO | ............... | 54 | ........ | 10·8 | ........ | 10·98 |
| $C^{42}H^{18}O^{22}$ + 6aq. | .... | 500 | ........ | 100·0 | | |

B. *Aqueous solution.* Euxanthic acid is nearly insoluble in cold water and rather more soluble [easily soluble (Stenhouse)] in boiling water (Erdmann).

C. *With Salifiable Bases.* — Euxanthic acid forms with bases salts represented by the formula $C^{42}H^{17}MO^{22}$: they frequently contain water of crystallisation, even after drying at 100°. Laurent's formulæ (*Compt. chim.* 1849, 377) here adopted differ from those of Gerhardt (*Traité,* 3, 768), in which the potash and ammonia-salts dried at 100° are supposed to be anhydrous.

The acid dissolves easily in caustic alkalis and their carbonates, eliminating carbonic acid from the latter. The euxanthates of the fixed alkalis and of ammonia dissolve very easily in pure water, but are nearly insoluble in strong solutions of alkaline carbonates (Erdmann). The aqueous acid does not precipitate salts of lime, baryta, strontia, magnesia, or silver (Stenhouse). The soluble salts of euxanthic acid form with most metallic salts yellow precipitates which are soluble in pure water but insoluble in the liquids in which they are formed. They precipitate *chloride of barium* and *calcium* yellowish white and gelatinous ; the *sulphates of manganese, nickel,* and *zinc,* lemon-yellow ; and throw down from *ferrous sulphate* a white precipitate quickly turning greenish brown, almost black, and from *ferric sulphate* a black-green precipitate. They precipitate *corrosive sublimate* yellowish, after some time only, and *nitrate of silver* yellowish and gelatinous, the latter precipitate turning brown on exposure to light, and dissolving when washed with cold water (Erdmann). — The salts of euxanthic acid are decomposed by mineral acids, and less completely by acetic acid, with separation of crystalline euxanthic acid. The solution of euxanthate of potash, mixed with a large excess of potash and heated to boiling, yields, on addition of hydrochloric acid, an amorphous semi-fluid precipitate, which partly floats on the liquid in oily drops, and is gradually transformed into crystalline euxanthic acid. When heated in an open vessel, the salts give off yellow vapours of euxanthone (Erdmann).

*Euxanthate of Ammonia.* — Crude euxanthic acid is treated with excess of strong aqueous carbonate of ammonia at a gentle heat, whereupon the acid dissolves, with evolution of carbonic acid. The solution on slightly cooling deposits an abundance of the crystalline ammonia-salt, which is nearly insoluble in excess of carbonate of ammonia ; it must be collected, washed with aqueous carbonate of ammonia, pressed, and dried over oil of vitrol. — Small, flat, yellow shining needles. At 120° it loses weight slowly and continuously (Erdmann).

|        |                          | Over oil of vitriol. |        |        |        | Erdmann. mean. |
|--------|--------------------------|---------|--------|--------|--------|---------|
| 42 C   | ........................ | 252     | ...... | 52·39  | ...... | 52·3    |
| N      | ........................ | 14      | ...... | 2·91   |        |         |
| 23 H   | ........................ | 23      | ...... | 4·78   | ...... | 4·7     |
| 24 O   | ........................ | 192     | ...... | 39·92  |        |         |

| C⁴²H¹⁷O²¹,NH⁴O + 2aq. .... | 481 | ...... | 100·00 |
|---|---|---|---|

*Euxanthate of Potash.* Obtained by dissolving euxanthic acid, with the aid of a gentle heat, in aqueous bicarbonate of potash, washing the pale crystalline scales deposited on cooling with aqueous carbonate of ammonia, to remove adhering carbonate of potash, pressing, and drying over oil of vitrol (Erdmann).

|       |                       | at 120°. |        |        |        | Erdmann. |
|-------|-----------------------|----------|--------|--------|--------|----------|
| 42 C  | ....................   | 252      | ...... | 50·22  | ...... | 49·81    |
| 19 H  | ....................   | 19       | ...... | 3·78   | ...... | 3·72     |
| 23 O  | ....................   | 184      | ...... | 36·61  | ...... | 36·84    |
| KO    | ....................   | 47·2     | ...... | 9·39   | ...... | 9·63     |

| C⁴²KH¹⁷O²² + 2aq. .... | 502·2 | ...... | 100·00 | ...... | 100·00 |
|---|---|---|---|---|---|

*Euxanthate of Magnesia.* Forms the principal constituent of purree. The aqueous acid and its ammonia-salt do not precipitate magnesia-salts, but a solution of sulphate of magnesia mixed with sal-ammoniac and ammonia produces in moderately dilute aqueous euxanthate of ammonia, a pale yellow slimy turbidity, and after a few minutes the mixture solidifies to a reddish-yellow transparent jelly, which afterwards becomes crystalline. Shining yellow crystalline powder, losing 13·95 p. c. of water at 130° (8 at. = 12·9 ; 10 at. = 15·6 p. c.). — In the crystalline state it is nearly insoluble in boiling water (Erdmann).

|        |                          | at 130°. |        |        |        | Erdmann. |
|--------|--------------------------|----------|--------|--------|--------|----------|
| 42 C   | ........................ | 252      | ...... | 51·85  | ...... | 51·83    |
| 18 H   | ........................ | 18       | ...... | 3·70   | ...... | 3·49     |
| 22 O   | ........................ | 176      | ...... | 36·21  | ...... | 35·80    |
| 2 MgO  | ........................ | 40       | ...... | 8·24   | ...... | 8·88     |

| C⁴²H¹⁷MgO²²,MgO,HO .... | 486 | ...... | 100·00 | ...... | 100·00 |
|---|---|---|---|---|---|

Erdmann found 9·2 and 9·57 p. c. MgO in another preparation.

*Euxanthate of Lead.* — **a.** *Basic.* — Obtained by precipitating alcoholic euxanthic acid with an alcoholic solution of neutral (or basic) acetate of lead, washing the orange-yellow, somewhat gelatinous precipitate repeatedly with boiling alcohol, and drying it at 100°. The salt melts when strongly heated, and yields a sublimate of euxanthone (Stenhouse).

|        |                          |       |        |        |        | Stenhouse. at 100°. |
|--------|--------------------------|-------|--------|--------|--------|----------|
| 42 C   | ........................ | 252   | ...... | 37·61  | ...... | 35·99    |
| 18 H   | ........................ | 18    | ...... | 2·69   | ...... | 3·01     |
| 22 O   | ........................ | 176   | ...... | 26·26  | ...... | 26·84    |
| 2 PbO  | ........................ | 224   | ...... | 33·44  | ...... | 34·16    |

| C⁴²H¹⁷PbO²²,PbO,HO .... | 670 | ...... | 100·00 | ...... | 100·00 |
|---|---|---|---|---|---|

**b.** *Neutral.* — Obtained in yellow spongy flocks by precipitating euxanthate of ammonia with nitrate of lead at the boiling heat (Erdmann).

| | | | | Erdmann. at 120°. | |
|---|---|---|---|---|---|
| 42 C | 252 | ........ | 45·90 | ........ | 44·78 |
| 17 H | 17 | ........ | 3·09 | ........ | 3·07 |
| 21 O | 168 | ........ | 30·60 | ........ | 31·43 |
| PbO | 112 | ........ | 20·41 | ........ | 20·72 |
| $C^{42}H^{17}PbO^{22}$ .... | 549 | ........ | 100·00 | ........ | 100·00 |

*Euxanthate of Copper.* — Sulphate of copper throws down from aqueous euxanthate of ammonia, at medium temperatures, a yellow gelatinous precipitate, which converts stronger solutions into a pasty mass, and settles in a pulverulent form when the liquid is heated. — After drying it is brown and triturable to a yellow powder. — In the moist state it dissolves freely in pure water, but not in presence of cupric sulphate (Erdmann).

Euxanthic acid dissolves very freely in boiling *alcohol* and *ether*. It is precipitated from its alcoholic solution in the crystalline form by water (Stenhouse).

Oxy-bromine-nucleus $C^{42}Br^{2}H^{16}O^{18}$.

## Bromeuxanthic Acid.

$$C^{42}Br^{2}H^{16}O^{22} = C^{42}Br^{2}H^{16}O^{18},O^{4}.$$
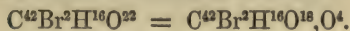
ERDMANN. *J. pr. Chem.* 37, 394.

*Acide euxanthique bibromé* (Laurent).

*Formation and Preparation.* Euxanthic acid suspended in water is agitated with excess of bromine, and the yellow pulverulent product is collected on a filter, washed with water and cold alcohol, and dissolved in boiling alcohol. On cooling the solution, the greater part is deposited, but a portion remains in solution, and is obtained as an amorphous acid on evaporation.

*Properties.* Yellow crystalline powder, giving off 3·1 to 4 p. c. of water at 130°. On evaporating the alcoholic solution, and sometimes also on precipitating the salts with hydrochloric acid, amorphous microscopic globules are obtained, which likewise occur mixed with the needles of the crystallised acid.

| | | | | Erdmann. | | |
|---|---|---|---|---|---|---|
| | at 130°. | | | Crystallised. (mean.) | | Amorphous. |
| 42 C | 252 | ........ | 41·72 | ........ | 40·56 | ........ 40·82 |
| 2 Br | 160 | ........ | 26·49 | ........ | 28·29 | ........ 27·48 |
| 16 H | 16 | ........ | 2·65 | ........ | 2·57 | ........ 2·66 |
| 22 O | 176 | ........ | 29·14 | ........ | 28·58 | ........ 29·04 |
| $C^{42}Br^{2}H^{16}O^{22}$ .... | 604 | ........ | 100·00 | ........ | 100·00 | ........ 100·00 |

Bromeuxanthic acid forms with *oil of vitriol* a solution from which water throws down bromeuxanthone in the form of a yellow powder. — With bases it forms *salts*, which are for the most part gelatinous.

The ammonia-salt is formed by dissolving the acid in aqueous ammonia. From this solution hydrochloric acid generally throws down the acid in the crystalline form ; but on one occasion Erdmann obtained a precipitate which deliquesced to a viscid syrup at 50°, and dried up to glassy amorphous particles, only slowly soluble in ammonia, and afterwards yielding the amorphous acid by precipitation with hydrochloric acid.

The solution of *bromeuxanthate of ammonia* immediately yields with *carbonate of ammonia*, a gelatinous precipitate, in which needles form after some time, till the entire precipitate becomes distinctly crystalline. The crystals, collected on a filter, dried over oil of vitriol, and dissolved in water, exhibit the following reactions. *Bicarbonate of potash* produces a yellow curdy precipitate, made up of tough threads ; *carbonate of soda* immediately forms a stiff jelly, which dissolves when heated, and re-appears in the non-crystalline state on cooling ; *chloride of barium* produces a yellow jelly in which microscopic globules are formed after some weeks ; *chloride of magnesium* mixed with sal-ammoniac and ammonia forms a yellow jelly ; *acetate of lead* an orange-yellow, and *sulphate of copper* a yellow jelly.

Amorphous bromeuxanthic acid dissolves in *alcohol* much more freely than the crystalline variety.

### Oxy-chlorine-nucleus  C⁴²Cl²H¹⁶O¹⁸.

## Chloreuxanthic Acid.

$$C^{42}Cl^2H^{16}O^{22} = C^{42}Cl^2H^{16}O^{18},O^4.$$
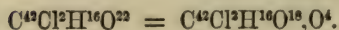
ERDMANN.   *J. pr. Chem.* 37, 392.

*Acide euxanthique bichloré.*

Euxanthic acid is suspended in water, and chlorine is passed through the liquid, till the acid no longer appears crystalline, and becomes flocculent. When the current of chlorine is continued too long, another product is formed (p. 532). When the flocks are collected on a filter and crystallised repeatedly from alcohol, unchanged euxanthic acid remains in the mother-liquors.

Golden-yellow, shining crystalline scales, which give off their water of crystallisation at 130°.

|  | at 130°. |  |  |  | Erdmann. |
|---|---|---|---|---|---|
| 42 C ................... | 252 | ........ | 48·93 | ........ | 48·64 |
| 2 Cl ................ | 71 | ........ | 13·79 | ........ | 14·41 |
| 16 H ................ | 16 | ........ | 3·11 | ........ | 3·08 |
| 22 O ................... | 176 | ........ | 34·17 | ........ | 33·87 |
| C⁴²Cl²H¹⁶O²² .... | 515 | ........ | 100·00 | ........ | 100·00 |

Erdmann's earlier formula was C⁴⁰Cl²H¹⁴O²¹. The above formula was proposed by Gerhardt (*N. J. Pharm.* 10, 158).

*Decompositions.* Chloreuxanthic acid forms with *oil of vitriol* a solution from which water throws down chloreuxanthone (p. 184) in the form of a yellow powder. The supernatant liquid is free from hydro-

chloric acid, but holds in solution, besides sulphuric acid, an acid containing chlorine and sulphur, and forming a soluble salt with baryta.

*Combinations.* Chloreuxanthic acid is insoluble in water.
It forms with bases the *chloreuxanthates*, which are gelatinous precipitates, or are thrown down as such when their aqueous solutions are mixed with excess of alkaline carbonates. The yellow solution of the acid in caustic ammonia is converted by caustic ammonia, the fixed alkalis, and their carbonates, into a transparent jelly, which afterwards becomes crystalline when carbonate of ammonia or potash has been employed. The ammoniacal solution yields orange-yellow gelatinous precipitates with *chloride of barium, acetate of lead, nitrate of nickel,* and *sulphate of copper;* yellow gelatinous precipitates with *sulphate of zinc* and *nitrate of silver;* a brown jelly with *ferric sulphate.* None of these precipitates afterwards become crystalline. They dissolve in a large quantity of water, and cannot, therefore, be washed.

Chloreuxanthic acid dissolves with difficulty in cold, freely in boiling *alcohol.*

*Oxy-nitro-nucleus* $C^{42}XH^{17}O^{18}$.

## Nitroeuxanthic Acid.

$$C^{42}NH^{17}O^{26} = C^{42}XH^{17}O^{18},O^4.$$
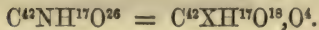
ERDMANN.  *J. pr. Chem.* 37, 400.

*Acide euxanthique nitré.*

Dry euxanthic acid dropped into cold nitric acid of sp. gr. 1·31 becomes converted in 24 hours into a pale-yellow granulo-crystalline deposit, surmounted by a yellowish-red liquid. The deposit is collected and dissolved in boiling alcohol, from which the greater part of the acid separates on cooling.

Microscopic, foliated crystals, of a pale straw-yellow colour.

|  |  | at 120°. |  |  | Erdmann. |
|---|---|---|---|---|---|
| 42 C | 252 | ........ | 51·32 | ........ | 50·75 |
| N | 14 | ........ | 2·85 | ........ | 3·23 |
| 17 H | 17 | ........ | 3·46 | ........ | 3·36 |
| 26 O | 208 | ........ | 42·37 | ........ | 42·66 |
| $C^{42}XH^{17}O^{22}$ | 491 | ........ | 100·00 | ........ | 100·00 |

Nitro-euxanthic acid, when heated with *nitric acid,* is converted into coccinonic acid, with simultaneous formation of oxalic acid (p. 532). It dissolves very slightly in *water.*

The *salts of nitroeuxanthic acid* explode when heated. — The acid dissolves in aqueous *carbonate of ammonia* and *carbonate of potash* with yellow colour: strong solutions solidify, on cooling, to a clear jelly, which gradually contracts and afterwards becomes crystalline. The jelly produced by caustic ammonia is transparent and quite amorphous. The neutral ammonia-salt forms with the *chlorides of barium* and

*calcium*, yellow precipitates, soluble in a large quantity of water; with *acetate of lead*, lemon-yellow; with *ferrous sulphate*, reddish-brown; with *ferric sulphate*, pale-brown; with *nitrate of nickel* and *sulphate of copper*, yellow; with *nitrate of silver*, orange-yellow. All these pre-cipitates are gelatinous.

*Nitroeuxanthate of Lead.* — The precipitate thrown down by acetate of lead from the ammonia-salt of nitroeuxanthic acid is washed with boiling water. It forms when dried a reddish-yellow glassy mass, having a conchoïdal fracture.

|  |  | at 120°. |  |  |  | Erdmann. |
|---|---|---|---|---|---|---|
| 42 C | .......................... | 252 | ........ | 35·24 | ........ | 34·84 |
| N | .......................... | 14 | ........ | 1·95 |  |  |
| 17 H | .......................... | 17 | ........ | 2·37 | ........ | 2·08 |
| 26 O | .......................... | 208 | ........ | 29·09 |  |  |
| 2 PbO | .......................... | 224 | ........ | 31·35 | ........ | 32·13 |
| $C^{42}XH^{16}PbO^{22},PbO,HO.$ | | 715 | ........ | 100·00 | | |

Nitroeuxanthic acid dissolves very slightly in *alcohol*, even at the boiling heat.

*Primary Nucleus $C^{42}H^{40}$; Oxygen-nucleus $C^{42}H^{24}O^{16}$.*

## Beta-erythrin.

$$C^{42}H^{24}O^{20} = C^{42}H^{24}O^{16},O^{4}.$$
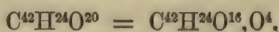
(Appendix to xiii, 150.)

MEŇSCHUTKIN. *Par. Soc. Bull.* 1864, 424; *Zeitschr. f. Chem.* 8, 112. LAMPARTER. *Ann. Pharm.* 134, 243.

Occurs in a dwarf variety of *Roccella fuciformis*, the ordinary varieties of which contain erythric acid (xii, 381).

*Preparation.* The lichen is digested in thin milk of lime for an hour at the ordinary temperature, the liquid is filtered, and the residue is pressed and again treated with milk of lime. The solutions are precipitated with dilute sulphuric acid, and the precipitate (which is heavier and less gelatinous than when thrown down by hydrochloric or carbonic acid, owing to admixed sulphate of lime) is washed, pressed, and exhausted with alcohol, from which beta-erythrin crystallises on careful evaporation (Lamparter). The alcoholic solution must not be heated above 40° or 50° (Menschutkin).

Air-dried beta-erythrin loses water of crystallisation at 100°.

*Properties.* White crystalline powder, or indistinctly crystalline globules. Scarcely reddens litmus. When dry it is permanent in the air. Melts at 115° to 116°, evolving carbonic acid copiously (Lamparter). Ordinary erythrin melts at 137°, and evolves carbonic acid only at temperatures above 200°.

| | | at 100°. | | | Menschutkin. mean. | | Lamparter. mean. |
|---|---|---|---|---|---|---|---|
| 42 C | .......... | 252 | ........ | 57·8 | ........ | 57·21 | ........ | 57·02 |
| 24 H | .......... | 24 | ........ | 5·5 | ........ | 5·71 | ........ | 5·72 |
| 20 O | .......... | 160 | ........ | 36·7 | ........ | 37·08 | ........ | 37·26 |
| $C^{42}H^{24}O^{20}$ | .... | 436 | ........ | 100·0 | ........ | 100·00 | ........ | 100·00 |

Lamparter supposes beta-erythrin dried at 100° still to contain 1 at. water. — Homologous with erythric acid (xii, 381) ?

*Decompositions.* 1. By fusion (see above). Beta-erythrin melts on platinum foil, and *burns* with bright flame when more strongly heated. — 2. Moist and impure beta-erythrin turns red in the *air*. — 3. When boiled with water it is resolved into orsellinic acid and beta-picro-erythrin :

$$C^{42}H^{24}O^{20} = C^{16}H^{8}O^{8} + C^{26}H^{16}O^{12}.$$
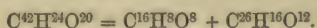
By boiling with strong alcohol, orsellinate of ethyl (xii, 373) is obtained instead of orsellinic acid. — 4. Solutions of beta-erythrin in aqueous *alkalis* leave on evaporation, amorphous products and carbonates, the beta-picroerythrin first formed being, doubtless, resolved into carbonic acid, erythroglucin, and beta-orcin. — 5. Beta-erythrin acquires a transient deep-red colour by contact with solution of *chloride of lime*. It reduces *nitrate of silver*.

*Combinations.* *With Water.* Crystallised beta-erythrin loses 4·60 p. c. (Lamparter), 4·51 p. c. of water at 100° (Menschutkin) (2 at. = 3·96 p. c. HO.).

It is nearly insoluble in water, but easily soluble in aqueous *alkalis* and *alkaline earths*.

*Basic acetate of lead* throws down from the (ammoniacal ?) solution a white jelly which cannot be obtained pure, even by prolonged wash-ing (Menschutkin).

| | | | | | Menschutkin. |
|---|---|---|---|---|---|
| 42 C | .................... | 252 | ........ | 29·72 | ........ | 27·54 |
| 20 H | .................... | 20 | ........ | 2·35 | ........ | 2·62 |
| 4 Pb | .............. | 416 | ........ | 49·05 | ........ | 49·40 |
| 20 O | .................... | 160 | ........ | 18·88 | ........ | 20·44 |
| $C^{42}H^{20}Pb^{4}O^{20}$ | .... | 848 | ........ | 100·00 | ........ | 100·00 |

Beta-erythrin dissolves easily in *alcohol* and *ether*.

## Appendix to xiii, 150.

# Beta-picroerythrin.

### $C^{26}H^{16}O^{12}$.
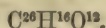
A solution of beta-erythrin in alcohol boiled for four or five hours, is no longer precipitable by water; and on distilling off the alcohol and dissolving the residue in water, orsellinate of ethyl crystallises out, whilst beta-picroerythrin remains in solution. The latter body is freed from traces of beta-orcin by treating it with ether, and may

be crystallised from solution in a very small quantity of boiling water.

Concentrically arranged needles, triturable to a very light powder. Has a slightly acid reaction.

| | | Dried at 100° or over oil of vitriol. | | | | Menschutkin. mean. |
|---|---|---|---|---|---|---|
| 26 C | ............... | 156 | ............ | 58·20 | ............ | 58·29 |
| 16 H | ............ | 16 | ............ | 5·97 | ............ | 6·34 |
| 12 O | ............... | 96 | ............ | 35·83 | ............ | 35·37 |
| $C^{26}H^{16}O^{12}$ | .... | 268 | ............ | 100·00 | ............ | 100·00 |

Differs from picroerythrin (xii, 380) in containing $C^{2}H^{2}$ more and 2HO less.

Beta-picroerythrin is resolved by boiling with a large quantity of *baryta-water* into carbonic acid, erythroglucin (xii, 385), and beta-orcin (xiii, 150). When a large excess of baryta is employed, these products are dark-coloured, but when the baryta is not in excess they are obtained nearly colourless. Beta-picroerythrin produces with *bromine-water* a yellow precipitate, soluble in ether; it is not affected by boiling *tincture of iodine.* — It assumes a transient red colour with *chloride of lime.* — *Nitrate of silver* throws down from ammoniacal beta-picroerythrin a reddish precipitate, from which the metal is reduced on warming.

Beta-picroerythrin dissolves very easily in *water*, aqueous *alkalis*, and *baryta-water*. The ammoniacal solution yields a white precipitate with basic acetate of lead. — It dissolves very easily in *alcohol*, very slightly in *ether* (Lamparter; Menschutkin).

### Primary Nucleus $C^{42}H^{42}$.

## Medullic Acid.

$$C^{42}H^{42}O^{4} = C^{42}H^{42},O^{4}.$$
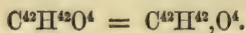
K. Eylerts.  *Pharm. Viertelj.* 9, 330; *N. Br. Arch.* 104, 129.

A fatty acid, which, according to Eylerts, occurs, together with palmitic and oleic acid, combined with glycerin, in beef-marrow. It is obtained by saponifying the fat, decomposing the soap, and treating the fatty acids according to Heintz's method (xvi, 210), going down in the first portions of the magnesian precipitates. Its melting-point is 72·5°, and is not raised by recrystallisation.

| | | at 50°. | | | Eylerts. | | |
|---|---|---|---|---|---|---|---|
| 42 C | ............ | 252 | ........ | 77·30 | ........ | 77·04 | ........ | 77·21 |
| 42 H | ............ | 42 | ........ | 12·88 | ........ | 12·98 | ........ | 12·89 |
| 4 O | ............ | 32 | ........ | 9·82 | ........ | 9·98 | ........ | 9·90 |
| $C^{42}H^{42}O^{4}$ | .... | 326 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

*Primary Nucleus* $C^{42}H^{44}$ ; *Oxygen-nucleus* $C^{42}H^{32}O^{12}$.

## Bryoretin.

$$\textbf{:}\, C^{42}H^{34}O^{14} = C^{42}H^{32}O^{12},H^2O^2.$$
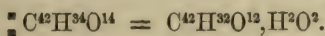
WALZ. *N. Jahrb. Pharm.* 9, 223.

Aqueous bryonin is resolved by boiling with dilute sulphuric acid into sugar and a yellow resin, which is separated by digestion with ether into a soluble portion, bryoretin, and an insoluble portion, *hydro-bryoretin.* Both bodies are amorphous.

| Bryoretin. | | | Walz. mean. | Hydrobryoretin. | | | Walz. mean. |
|---|---|---|---|---|---|---|---|
| 42 C ........... | 63·16 | .... | 63·23 | 42 C ... ........ | 60·43 | .... | 59·97 |
| 35 H ........... | 8·77 | .... | 8·80 | 37 H ........... | 8·87 | .... | 9·36 |
| 14 O ........... | 28·07 | .... | 27·97 | 16 O ........... | 30·70 | .... | 30·67 |
| $C^{42}H^{35}O^{14}$ .... | 100·00 | .... | 100·00 | + 2HO .... | 100·00 | .... | 100·00 |

*Glucoside of Bryoretin.*

## Bryonin.

G. F. WALZ. *N. Jahrb. Pharm.* 2, 65, and 217; *N. Br. Arch.* 96, 150; *Chem. Centr.* 1859, 5; *Pharm. Viertelj.* 7, 550. — *N. Jahrb. Pharm.* 16, 8.

The bitter principle of *Bryonia alba* (Handbuch, viii [2], 37). — The substance formerly described as *Bryonitin* is, according to Walz's later statements, a mixture containing fat.

Vitalis, Frémy, and Chevallier (*J. Chim. méd.* 1, 345) described as bryonin, a bitter, indistinctly crystalline body soluble in water, obtained by precipitating the sap of the root of *Bryonia alba* with ammonia, and evaporating the filtrate. Vauquelin (*Ann. du Mus.* 8, 80; *Berl. Jahrb.* 1807, 14) and Dulong (*J. Pharm.* 12, 158) described under the same name the portion of the inspissated sap soluble in alcohol and water. Brandes & Firnhaber (*Br. Arch.* 3, 356) precipitated the aqueous solution of the alcoholic extract with basic acetate of lead, evaporated the filtrate freed from lead, and described as bryonin the portion of the residue soluble in alcohol, but obtained no substance exhibiting characteristic reactions. They found also in bryony root a resin soluble, and another resin insoluble in ether.

Schwerdtfeger (*Jahrb. pr. Pharm.* 7, 228) obtained from the fresh root of *Bryonia dioïca* (by exhausting it with water and alcohol, precipitating with basic acetate of lead, and decomposing the precipitate with hydrosulphuric acid) tufts of pearly needles containing nitrogen, and having a bitter and acrid taste. The body dissolves in water and dilute acids, from which it is precipitated by ammonia, and is soluble also in alcohol, but not in ether.

*Preparation.* An alcoholic extract of the dried root is exhausted with cold water; the solution is precipitated with basic acetate of lead and filtered; and the filtrate, freed from lead by hydrosulphuric acid, is neutralised with carbonate of soda and precipitated by tannic acid. The precipitate thus obtained is dissolved in alcohol and decomposed by digesting it for some hours with quick-lime suspended in alcohol; after which the solution containing bryonin is filtered, decolorised with animal charcoal, and evaporated. The residue is purified by washing with ether, and by again dissolving it in alcohol, precipitating with tannic acid, and decomposing the precipitate with quick-lime.

Colourless, very bitter mass, triturable to a white powder.

| *Calculation according to Walz.* | | | | | | Walz. | | |
|---|---|---|---|---|---|---|---|---|
| 96 C ............ | 576 | ........ | 60·00 | ........ | 59·72 | to | 60·11 |
| 80 H ............ | 80 | ........ | 8·33 | ........ | 8·28 | ,, | 8·51 |
| 38 O ............ | 304 | ........ | 31·67 | ........ | 32·00 | ,, | 31·38 |
| C⁹⁶H⁸⁰O³⁸ .... | 960 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Bryonin is resolved by boiling with dilute *acids* into sugar, bryoretin, and hydrobryoretin. According to Walz thus:

$$C^{96}H^{80}O^{38} + 4HO = C^{42}H^{35}O^{14} + C^{42}H^{37}O^{16} + C^{12}H^{12}O^{12}.$$
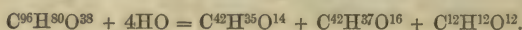
100 parts of bryonin yielded 17·8 parts of grape-sugar, as calculated from the amount of cuprous oxide thrown down. — It is coloured red-brown by *oil of vitriol*, whereupon water produces a white precipitate. — Fuming *nitric acid* produces a substance insoluble in water. — Bryonin does not reduce *alkaline solutions of cupric oxide.*

Bryonin dissolves easily in *water* and in 2 or 3 parts of *alcohol*, but not in *ether.* The aqueous solution precipitates *bichloride of platinum* and *tannic acid* (Walz).

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# COMPOUNDS CONTAINING 44 ATOMS OF CARBON.

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*Primary Nucleus* C⁴⁴H³²; *Oxygen-nucleus* C⁴⁴H²⁰O¹².

## Brasilin or Sapan-red.

$$C^{44}H^{20}O^{14} = C^{44}H^{20}O^{12},O^2.$$
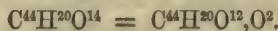
BOLLEY. *Züricher Mitth.* 1865, 2; *J. pr. Chem.* 93, 351; *Zeitschr. f. Chem.* 8, 192.

The colouring matter of sapan-wood (from *Cæsalpinia Sapan*) and of Brazil-wood (from *Cæsalpinia Crista, C. brasiliensis*, and other species). Discovered by Chevreul, and erroneously regarded at p. 287, vol. xvi, as hæmatoxylin.

*Preparation.* From the crystalline deposit which had formed in a vessel filled with extract of sapan-wood. It is not obtained pure, or

only with difficulty, from Brazil-wood. The deposit is dissolved in absolute alcohol and the filtrate is left to crystallise without exposure to air or light.

*Properties.* Amber-yellow to brownish rhombohedrons, or short oblique rhombic prisms.

| | | | | | Bolley. mean. |
|---|---|---|---|---|---|
| 44 C ................ | 264 | ........ | 66·66 | ........ | 66·61 |
| 20 H ............ | 20 | ........ | 5·06 | ........ | 5·00 |
| 14 O ................ | 112 | ........ | 28·28 | ........ | 28·39 |
| $C^{44}H^{20}O^{14}$ .... | 396 | ........ | 100·00 | ........ | 100·00 |

Differs from hæmatoxylin by containing the elements of carbolic acid more than that body.

With *nitric acid* it yields picric acid.

*Combinations.* — *Hydrated Brasilin.* — A solution of brasilin in weak spirit or aldehyde, yields small straw-yellow or golden-yellow needles, belonging to the oblique prismatic or monoclinic system; they turn brown and give off 6·61 p. c. of water at 90°, and no more at 120° (3 at. = 6·39 p. c. HO).

| | Needles. | | | | Bolley. |
|---|---|---|---|---|---|
| 44 C ........................... | 264 | ........ | 62·41 | ........ | 62·78 |
| 23 H ........................ | 23 | ........ | 5·43 | ........ | 5·45 |
| 17 O ........................... | 136 | ........ | 32·16 | ........ | 31·77 |
| $C^{44}H^{20}O^{14} + 3aq.$ .... | 423 | ........ | 100·00 | ........ | 100·00 |

Brasilin is soluble in *water*. The reddish solution is coloured deep carmine-red by traces of *ammonia, fixed alkalis,* or *baryta-water.* By slow evaporation of the alcoholic solution in air containing ammonia, spangles having the lustre of cantharides are obtained, which evolve ammonia when treated with caustic potash. — A solution of brasilin in aqueous bisulphite of soda yields colourless crystals containing sulphur.

Brasilin is soluble in *alcohol* and *ether*.

*Primary Nucleus* $C^{44}H^{34}$; *Oxyazo-nucleus* $C^{44}NH^{21}O^{12}$.

# Hydrastine.

$$C^{44}NH^{23}O^{12} = C^{44}NH^{21}O^{12},H^2.$$
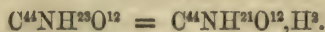
DURAND. *Amer. Pharm. Journ.* 23, 112 ; *N. Jahrb. Pharm.* 18, 143.
J. D. PERRINS. *Pharm. Journ.* [2] 3, 546; *N. Repert.* 11, 304; abstr. *N. Jahrb. Pharm.* 18, 143; *Chem. Centr.* 1862, 552 ; *Kopp's Jahresber.* 1862, 381.
MAHLA. *Sill. Amer. J.* 86, 57 ; *J. pr. Chem.* 91, 248; *Zeitschr. f. Chem.* 7, 287.

Observed by Durand in 1851, but first investigated and shown to be an independent body by Perrins. — Occurs, together with berberine, in the root of *Hydrastis canadensis*, a North American plant of the ranunculaceous order.

The mother-liquor obtained in the preparation of berberine (p. 187) is diluted with a large quantity of water and freed from alcohol, and ammonia is cautiously added to it till the precipitate produced remains constant, whereby resins are thrown down. The filtrate, mixed with a slight excess of ammonia, deposits hydrastine as a fawn-coloured precipitate, which is washed and purified by crystallisation from alcohol, with the aid of a little animal charcoal (Perrins). — Durand treats the aqueous extract of the root with magnesia, and boils the precipitate with alcohol, from which the hydrastine crystallises on spontaneous evaporation. Hydrastine may also be obtained by exhausting the root with chloroform, ether, or benzene (Perrins). The yield is about 1½ p. c. of the dried root (Perrins).

*Properties.* White, highly lustrous four-sided prisms, belonging to the monoclinic system (Mahla), becoming opaque on drying. Melts a little above 100° (Perrins), at 135° (Mahla) to a colourless resin. Has an alkaline reaction (Durand). Tasteless (Mahla); tastes bitter and narcotic, especially in its soluble compounds. It produces no particular effect on rabbits in doses of 5 grains (Perrins).

|        |      | at 100° |        |        | Mahla. mean. |
|--------|------|---------|--------|--------|--------------|
| 44 C   | .............. | 264 | ........ | 66·49 | ........ | 66·54 |
| N      | .............. | 14  | ........ | 3·53  | ........ | 3·80  |
| 23 H   | .............. | 23  | ........ | 5·76  | ........ | 5·85  |
| 12 O   | .............. | 96  | ........ | 24·22 | ........ | 23·81 |
| C⁴⁴NH²³O¹² | ........ | 397 | ........ | 100·00 | ........ | 100·00 |

Mahla's formula contains 1 at. hydrogen more.

*Decompositions.* Hydrastine when strongly heated evolves yellowish vapours and an odour of carbolic acid (Mahla). — When heated on platinum-foil it *burns* with smoky flame (Mahla). — When moistened with *nitric acid,* it turns yellowish-brown (Perrins), and dissolves with red colour (Mahla). — It dissolves in *oil of vitriol,* forming a yellow solution, which turns red when warmed; the latter solution is turned brown by chromate of potash (Mahla). Oil of vitriol together with chromate of potash or peroxide of lead, colours hydrastine a brick-red, different from the purple-red of strychnine (Perrins). — *Chlorine-water* produces a blue iridescence in the aqueous salts (Perrins). — Boiling potash-ley does not act upon hydrastine (Mahla).

Hydrastine is insoluble or nearly so in *water.* — It forms with acids easily soluble, very bitter non-crystalline salts. The phosphate and iodate are less easily soluble. Double salts are obtained with gold, mercury, and platinum (Perrins). The salts are precipitated white by alkalis. The granular precipitate thrown down by ammonia is quickly transformed into crystals (Perrins). The salts are precipitated white by iodide of potassium and ferrocyanide of potassium, yellow by chromate of potash, brown by biniodide of potassium (Mahla).

*Hydrochlorate of Hydrastine.* — The easily formed solution of hydrastine in dilute hydrochloric acid leaves on evaporation, an amorphous gum, the aqueous solution of which exhibits a blue fluorescence (Mahla).

| | *at 100°.* | | | Mahla. | |
|---|---|---|---|---|---|
| $C^{44}NH^{23}O^{12}$ ............ | 397·0 | ........ | 91·58 | | |
| HCl ................... | 36·5 | ........ | 8·42 | ........ | 8·48 |

| $C^{44}NH^{23}O^{12}$,HCl .... | 433·5 | ........ | 100·00 |
|---|---|---|---|

*Terchloride of gold* throws down from hydrochlorate of hydrastine a reddish-yellow precipitate, which melts to a resin when heated, and afterwards dissolves (Mahla).

*Chloroplatinate of Hydrastine.* — Yellowish-red precipitate containing 16·17 p. c. of platinum (calc. for $C^{44}NH^{23}O^{12}$,HCl,PtCl$^2$ requires 16·36 p. c. Pt) (Mahla).

*Picrate of Hydrastine* dissolves with difficulty in strong alcohol, and crystallises from the solution in needles having the aspect of wavellite (Perrins).

Hydrastine dissolves easily in *alcohol, ether, chloroform,* and *benzene.*

*Primary Nucleus* $C^{44}H^{36}$ ; *Oxygen-nucleus* $C^{44}H^{34}O^2$.

# Gurgunic acid.

$$C^{44}H^{34}O^8 = C^{44}H^{34}O^2,O^6.$$
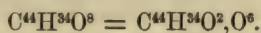
C. WERNER. *Zeitschr. Ch. Pharm.* 1862, 588; *Chem. Centr.* 1863, 202; *Kopp's Jahresber.* 1862, 461.

A constituent of wood-oil or gurguna balsam, a product imported from Calcutta, and obtained from various species of Dipterocarpus.

When the reddish-brown balsam is distilled with water, a volatile oil, $C^{40}H^{32}$, passes over, whilst the acid remains behind, together with other constituents. The residue is dissolved in boiling potash-ley; the red-brown solution is mixed with excess of sal-ammoniac and filtered; and the filtrate is precipitated with hydrochloric acid. The acid, which is thrown down in dense yellow flocks, is dissolved by shaking the liquid with ether, and is obtained, on evaporating the ethereal layer, in the form of a crust, which is purified by repeated crystallisation from alcohol.

*Properties.* Colourless, crumbly, opaque crystalline crusts. Melts at 220° and solidifies in a crystalline mass at 180°. Colours litmus wine-red.

| | *at 100—120°.* | | | Werner. mean. |
|---|---|---|---|---|
| 44 C ............... | 264 | ........ | 72·91 | ........ 72·62 |
| 34 H ............ | 34 | ........ | 9·40 | ........ 9·65 |
| 8 O ............... | 64 | ........ | 17·69 | ........ 17·73 |

| $C^{44}H^{34}O^8$ ....... | 362 | ........ | 100·00 | ........ | 100·00 |
|---|---|---|---|---|---|

*Decompositions.* The acid *boils* at 260°, and yields as distillate an amorphous mass, the alcoholic solution of which turns yellow in the air. — It is decomposed by *nitric acid,* and carbonised by *oil of vitriol.*

It remains unchanged in boiling *water.*

The acid is *bibasic,* but only its neutral salts, $C^{44}H^{32}M^2O^8$, are known.

— It dissolves easily in aqueous *ammonia*, and forms soaps with the *alkalis*. The remaining salts are insoluble.

*Potash-salt.* — Obtained from its alcoholic solution in deliquescent laminæ. Contains 18·16 p. c. of potassium, or rather more than corresponds to the formula $C^{44}H^{32}K^2O^8$ (17·88 p. c. K), on account of the admixture of carbonate.

*Baryta-salt.* — Obtained by pouring a hot ammoniacal solution of the acid into excess of dilute chloride of barium, and drying the product in the air, and afterwards at 100°—120°. — White amorphous precipitate, slightly soluble in water.

|  |  |  |  |  | Werner. mean. |
|---|---|---|---|---|---|
| 88 C | 528 | ........ | 55·90 | ........ | 55·26 |
| 67 H | 67 | ........ | 7·09 | ........ | 6·72 |
| 3 Ba | 205·5 | ........ | 21·77 | ........ | 22·05 |
| 18 O | 144 | ........ | 15·24 | ........ | 15·97 |
| $2C^{44}H^{32}O^6,3(BaO,HO)$ | 944·5 | ........ | 100·00 | ........ | 100·00 |

*Lime-salt.* — Resembles the baryta-salt.

|  |  |  |  | Werner. |
|---|---|---|---|---|
| $C^{44}H^{32}O^8$ | 360 | ........ | 90 |  |
| 2 Ca | 40 | ........ | 10 | ........ 10·04 |
| $C^{44}H^{32}Ca^2O^8$ | 400 | ........ | 100 |  |

The ammonia-salt forms with *cupric salts*, a fine blue precipitate, which quickly assumes a chrome-green colour. — It throws down a flocculent precipitate from *bichloride of platinum*.

*Silver-salt.* — White flocks, turning slightly red-brown in the light. Dissolves slightly in water.

|  |  |  |  |  | Werner. mean. |
|---|---|---|---|---|---|
| 44 C | 264 | ........ | 45·83 | ........ | 45·60 |
| 32 H | 32 | ........ | 5·55 | ........ | 5·59 |
| 2 Ag | 216 | ........ | 37·52 | ........ | 37·48 |
| 8 O | 64 | ........ | 11·10 | ........ | 11·33 |
| $C^{44}H^{32}Ag^2O^8$ | 576 | ........ | 100·00 | ........ | 100·00 |

The acid dissolves easily in strong *alcohol*, but not in alcohol of 75 p. c. It dissolves easily in *ether*, slowly in *benzene*, and with difficulty in *bisulphide of carbon*.

<center>*Primary Nucleus* C⁴⁴H³⁸; *Oxygen-nucleus* C⁴⁴H²⁶O¹².</center>

# Limonin.

$$? \; C^{44}H^{28}O^{14} = C^{44}H^{26}O^{12},O^2.$$
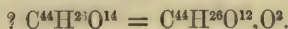
BERNAYS. *Repert.* 71, 306.
K. SCHMIDT. *Ann. Pharm.* 51, 338; *J. pr. Chem.* 33, 51.

*Limone.* Occurs in the pips of lemons and apples.

*Preparation.* The pips, beaten to a pulp with water, are exhausted with cold alcohol. The tincture thus obtained deposits the limonin on standing, in the form of a white powder and crystalline laminæ (Bernays).

*Properties.* White powder, made up of microscopic rhombic crystals. It does not alter at 200°, but melts at 240° to a yellow transparent resin, which solidifies to an amorphous mass on cooling, and crystallises again from acetic acid. Neutral. It has a strong pure bitter taste, and is without action on the organism in doses of 60 milligrammes (Schmidt).

|        |     | at 120°. |        |        |        | Schmidt. mean. |
| ------ | --- | -------- | ------ | ------ | ------ | -------------- |
| 44 C   | ....... | 264  | ........ | 65·67  | ........ | 65·98 |
| 26 H   | ........... | 26 | ........ | 6·48   | ........ | 6·53 |
| 14 O   | ............... | 112 | ........ | 27·85  | ........ | 27·49 |
| $C^{44}H^{26}O^{14}$ | .... | 402 | ........ | 100·00 | ........ | 100·00 |

The above is the formula given by Weltzien. (*System. Zusammenst.* 666); according to Schmidt it is $C^{42}H^{25}O^{13}$.

Limonin dissolves very slightly in *water*. It dissolves in *oil of vitriol*, forming a blood-red solution, from which it is precipitated unaltered by water, without forming a conjugated acid. The yellow solution in warm strong *nitric acid*, even after standing for some time, deposits the limonin unchanged, on addition of water. Limonin is not affected by boiling with *chromate of potash and sulphuric acid.* — It is insoluble in aqueous *ammonia*, but easily soluble in *potash-ley*, from which it is precipitated by acids (Schmidt).

Limonin dissolves easily in *alcohol* and in *acetic acid*, but very slightly in *ether* (Schmidt). The alcoholic solution is precipitated by *tannic* and *picric acids* (Bernays).

*Appendix to Limonin.*

## Hesperidin.

LEBRETON.　*J. Pharm.* 14, 377 ; *Repert.* 31, 261.
JONAS.　*N. Br. Arch.* 27, 186.
LEPAGE.　*J. Chim. méd.* 17, 583.
LANDERER.　*Repert.* 52, 215.

Discovered by Lebreton in 1828. — Occurs in sweet and bitter oranges and lemons, both ripe and unripe, more especially in the white spongy portion of oranges, the juice which exudes on cutting through the fruit being rendered milky by hesperidin. It occurs abundantly in the germs of orange-blossom, but not in the petals or filaments.

Plisson (*J. Pharm.* 15, 156) found hesperidin in a resinous mass, which was deposited from oil of lemons ; he may, however, have confounded it with bergaptene (xiii, 345). Crystals from oil of bergamot, described by Ricker (*Jahrb. pr. Pharm.* 14, 326), are probably bergaptene.

Widnmann's hesperidin (see below) appears to differ from that of Lebreton.

*Preparation.* The white part of unripe oranges, freed from the outer green peel and the inner portion, is exhausted with water, at a temperature of 25° to 30°; and the filtrate is concentrated, separated from the albumin which is deposited, neutralised with lime-water, and evaporated to a syrup, which is repeatedly treated with alcohol of 40°B., whereby gum, albumin, salts, and other matters are left behind. The alcoholic tincture yields on evaporation a very bitter granular extract, which on standing for a week with 20 times its weight of water or distilled vinegar, gradually deposits crystalline hesperidin. Purification is effected by recrystallisation from hot alcohol (Lebreton). — When unripe oranges are preserved in vinegar or alcohol of 22° B., hesperidin crystallises at the bottom of the vessel (Lebreton ; Landerer). Hesperidin is also deposited in white nodules from a very strong tincture of curassao-shells on standing for six weeks (Lepage).

The mother-liquor of hesperidin contains in solution the *bitter principle of oranges*, which is obtained on evaporation as a brown extract, the aqueous solution of which is coloured bright-yellow by ammonia, brown-red by ferric sulphate, and is not precipitated by gelatin. It dissolves in alcohol, but not in ether (Lebreton).

*Properties of Hesperidin.* — Very delicate, silky tufts of needles, grouped in nodules ; inodorous ; tasteless at first, afterwards bitter, probably owing to adhering bitter substance. Neutral (Lebreton). According to Lepage, it is tasteless ; according to Landerer, bitter and acid. It is phosphorescent when gently warmed (Bonastre).

*Decompositions.* 1. Hesperidin melts above 109°, and solidifies on cooling to a brownish-yellow transparent mass, which tastes bitter and sweet, and does not again crystallise from alcohol. — When submitted to *dry distillation*, it does not yield ammonia, but leaves a porous charcoal. — 2. It *burns* on red-hot charcoal, giving off fumes and a slightly aromatic odour. — 3. In cold *nitric acid* it assumes a yellowish-red, afterwards a permanent orange yellow colour, and dissolves when heated, forming a brown-red solution, changing to pale-yellow, with formation of oxalic acid and a little yellow artificial bitter. — 4. *Oil of vitriol* turns hesperidin first orange-yellow, afterwards bright red, changing in 12 hours to a rusty colour ; the red solution is rendered pale-yellow by water (Lebreton). Hesperidin is precipitated unchanged from its orange-yellow solution in oil of vitriol by water (Jonas). — 5. In strong *hydrochloric acid,* hesperidin acquires a greenish-yellow colour, which is destroyed by water (Lebreton). Hydrochloric acid does not affect solid hesperidin, but on boiling the alkaline solution with excess of hydrochloric or sulphuric acid, a deep orange-red resin is deposited, which is soluble in water, insoluble in alcohol, soluble in oil of vitriol with rose colour, in ammonia with greenish-yellow, and in caustic alkali with deep-red colour (Jonas).

*Combinations.* Hesperidin is nearly insoluble in cold, soluble in 60 parts of boiling *water,* which deposits ⅗ths of the amount dissolved on cooling. — It is insoluble in dilute *sulphuric* or *hydrochloric* acid, but easily soluble in aqueous *fixed alkalis* (Lebreton); also in aqueous *ammonia,*

remaining free from ammonia on evaporating the solution (Jonas); it is precipitated from the alkaline solutions by acids (Lepage). It forms with *lime* a soluble compound, precipitable by alcohol (Jonas).

The aqueous solution of hesperidin does not precipitate *neutral* or *basic acetate of lead.* According to Lebreton, it precipitates *ferric sulphate* brown-red; but according to Plisson, it does not.

Hesperidin dissolves slightly in cold, and freely in hot *glacial acetic acid.* The solution is not rendered turbid by water (Lebreton), but is precipitated by alcohol (Jonas); it leaves hesperidin free from acetic acid on evaporation (Lebreton).

It dissolves very sparingly in cold, very easily in hot *alcohol;* the solution is rendered only slightly turbid by water. — It is insoluble in cold and hot *ether,* and in *volatile* and *fat oils* (Lebreton).

Widmann's *Hesperidin* is likewise obtained from unripe oranges. — The sliced peel of the green fruit is digested in alcohol of sp. gr. 0·900, whereupon, after standing for six weeks, the liquid is found to contain laminæ floating in it. These laminæ, when recrystallised form four-sided glassy transparent prisms, bevelled with two faces. The crystals crunch between the teeth, and have a faint sweetish taste. They are inodorous, and have an acid reaction, and when heated melt and decompose, leaving charcoal. — Decomposed by strong *nitric acid,* with formation of oxalic acid. Dissolves in cold *oil of vitriol,* carbonising when heated.

Dissolves in 40 parts of cold, and in 10 parts of boiling *water,* forming a solution, which is slowly precipitated by *basic acetate,* but not by *neutral acetate of lead.* — Nearly insoluble in *alcohol,* either cold or boiling, which precipitates it in laminæ from the aqueous solution. — Insoluble in *ether,* and in *oils* both fat and *volatile* (Widmann, *Repert.* 32, 207).

## Primary Nucleus $C^{44}H^{42}$.

# Erucic Acid.

$$C^{44}H^{42}O^4 = C^{44}H^{42},O^4.$$
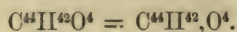
St. Darby. *Ann. Pharm.* 69, 1; *Pharm. Centr.* 1849, 177; *Chem. Gaz.* 1849, 163; *Kopp's Jahresber.* 1849, 347.

F. Websky. *J. pr. Chem.* 58, 449; *Pharm. Centr.* 1853, 808; *Kopp's Jahresber.* 1853, 443.

Städeler. *Ann. Pharm.* 87, 133; *Pharm. Centr.* 1853, 811; *J. pr. Chem.* 61, 374; *Kopp's Jahresber.* 1853, 445.

R. Otto. *Ann. Pharm.* 127, 183; abstr. *J. pr. Chem.* 90, 316; *Chem. Centr.* 1864, 111; *Répert. Chimie pure,* 6, 148; *N. J. Pharm.* 45, 103; *Kopp's Jahresber.* 1863, 335. — *Zeitschr. Ch. Pharm.* 8, 276; *Ann. Pharm.* 135, 226.

*Brassic acid.* — Occurs in the fat oil of black and white mustard-seed (Darby). In rape oil (Websky).

*Preparation.* A. *From fatty oil of mustard.* The fatty acids, obtained by saponifying the oil, salting out, and decomposing the

soap, are digested over the water-bath with finely triturated oxide of lead; the plaster thereby formed is exhausted with ether, which takes up oleate of lead; and the insoluble residue is decomposed with alcoholic hydrochloric acid. On distilling off the alcohol, erucic acid remains behind, and may be purified by repeated crystallisation from alcohol (Darby). — Otto saponifies the fat oil of white mustard-seed with oxide of lead, and treats the plaster with ether, which, according to him, but contrary to Darby's statement, dissolves the lead-salt of erucic acid. He then mixes the ethereal solution with hydrochloric acid, removes the chloride of lead thereby formed, evaporates the solution over the water-bath, and purifies the residue, which solidifies in the cold, by washing with water and recrystallisation from alcohol.

B. *From Rape-oil.* The fatty acids obtained by decomposing the soap with hydrochloric acid, and afterwards completely freed from the acid, are dissolved in an equal bulk of alcohol of sp. gr. 0·835; the solution is cooled to 5°, and left to crystallise; and the crystals are separated and pressed. The crystals are again crystallised three times from their own weight of alcohol, at last at a temperature of 10°, and pressed, and are finally melted with water to remove alcohol (Websky).

*Properties.* White, shining, very thin needles, often an inch long, melting at 34° [33° to 34° (Otto)], and solidifying at 33° (Darby). Long white, tasteless, and inodorous needles, arranged in masses resembling wavellite, melting at 32° to 33°, and solidifying at a somewhat lower temperature. The melted mass has a glassy lustre, and a lamellar fracture, with large cavities. Has an acid reaction. Permanent in the air (Websky).

|  |  |  |  |  | Darby. mean. |  | Websky. mean. |  | Otto. mean. |
|---|---|---|---|---|---|---|---|---|---|
| 44 C | ............ | 264 | ........ | 78·11 | ........ | 77·53 | ........ | 78·25 | ........ | 77·90 |
| 42 H | ........... | 42 | ........ | 12·43 | ........ | 12·60 | ........ | 12·56 | ........ | 12·55 |
| 4 O | ............ | 32 | ........ | 9·46 | ........ | 9·87 | ........ | 9·19 | ........ | 9·55 |
| C⁴⁴H⁴²O⁴ | .... | 338 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

Websky proposed the formula $C^{45}H^{43}O^4$, which Städeler, who recognised the identity of the two acids, altered to the above. — The melting-point of the acid is not altered by repeated crystallisation, and is the same in the portions of the acid which solidify first and in those which crystallise afterwards. Partial precipitation with neutral acetate of lead also fails to yield any portion having a different melting-point (Darby; Websky).

*Decompositions.* 1. The acid when exposed to the *air* gradually becomes coloured, and turns rancid (Otto). When heated to 100° for several days it assumes a yellow to brown colour, afterwards melts at a lower temperature, and solidifies to a tallowy mass after melting. During this change it acquires an aromatic odour, and at first becomes a little heavier, but afterwards (especially at 130°) loses weight (Websky). —2. With *bromine* it forms bromerucic acid, without elimination of hydrobromic acid (Otto).—3. It is converted by *nitrous acid* (not by sulphurous acid) into an isomeric crystalline acid (the *erucadic acid* of this Handbook) (Websky). Otto did not observe any change in the acid, which exhibited the same melting-point after treatment with nitrous acid as before. — 4. It is decomposed by fused *hydrate of potash*, with evolution of hydrogen; the products of decomposition include neither acetic nor

arachidic acid (p. 370) (Otto). — 5. On passing *hydrochloric acid gas* into alcoholic erucic acid, an oil is produced, which crystallises below 0°, and contains 77·05 p. c. C., and 12·00 H. (Otto).

*Soda-salt.* — Obtained in the same way as laurate of soda (xv, 47). — Slightly yellow crusts, unalterable at 110°. The solution in absolute alcohol forms a jelly on cooling (Websky).

|  |  |  |  |  | Websky. |
|---|---|---|---|---|---|
| 44 C ...................... | 264 | ........ | 73·33 | ........ | 73·77 |
| 41 H.................... | 41 | ........ | 11·39 | ........ | 11·39 |
| 3 O...................... | 24 | ........ | 6·67 | ........ | 6·36 |
| NaO ............ | 31 | ........ | 8·61 | ........ | 8·48 |
| $C^{44}H^{41}NaO^4$ .... | 360 | ........ | 100·00 | ........ | 100·00 |

*Baryta-salt.* — An alcoholic solution of the soda-salt throws down from alcoholic acetate of baryta white flocks (Darby), which crystallise from alcohol in small nodules (Otto). It softens at 75°, and turns yellow at 100°, giving off an odour and increasing in weight (Websky).

| *Dried over oil of vitriol or in vacuo.* |  |  |  |  | Darby. |  | Otto. |
|---|---|---|---|---|---|---|---|
| 44 C .... ............ | 264 | ........ | 65·09 | ........ | 64·36 | ........ | 65·00 |
| 41 H ................ | 41 | ........ | 10·11 | ........ | 10·40 | ........ | 10·10 |
| 3 O ................ | 24 | ........ | 5·92 | ........ | 6·34 | ........ | 6·12 |
| BaO ............ | 76·6 | ........ | 18·88 | ........ | 18·90 | ........ | 18·78 |
| $C^{44}H^{41}BaO^4$ .... | 405·6 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

*Lead-salt.* Precipitated from a solution of the soda-salt by alcoholic neutral acetate of lead (Darby). The (moist ? Kr.) lead-salt softens at 60°, and liquefies at 80° (Websky). It is insoluble in ether. See p. 550.

| *Dried in vacuo.* |  |  |  |  | Darby. |
|---|---|---|---|---|---|
| 44 C ...................... | 264 | ........ | 59·87 | ........ | 59·7 |
| 41 H ................ | 41 | ........ | 9·29 | ........ | 9·3 |
| 3 O ...................... | 24 | ........ | 5·44 | ........ | 5·6 |
| PbO ............ | 112 | ........ | 25·40 | ........ | 25·4 |
| $C^{44}H^{41}PbO^4$ .... | 441 | ........ | 100·00 | ........ | 100·00 |

Websky found varying amounts of oxide of lead in the salt washed with hot water.

*Silver-salt.* Thrown down from the alcoholic ammonia-salt by nitrate of silver, as a curdy precipitate, which soon turns dark and must be dried in a vacuum (Darby). The precipitate thrown down from the soda-salt immediately turns brown-red (Websky).

|  |  |  |  |  | Darby. |
|---|---|---|---|---|---|
| $C^{41}H^{41}O^3$ ........ | 329 | ........ | 74 |  |  |
| AgO ........ | 116 | ........ | 26 | ........ | 25·7 to 26 |
| $C^{44}H^{41}AgO^4$ .... | 445 | ........ | 100 |  |  |

Erucic acid dissolves very easily in *alcohol* and in *ether* (Websky).

# Erucadic Acid.

$$C^{44}H^{42}O^4 = C^{44}H^{42},O^4.$$
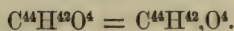
WEBSKY.  *J. pr. Chem.* 58, 459.

Erucic acid absorbs nitrous acid gas, becoming yellow and odorous, and when recrystallised from cooled alcohol, yields erucadic acid, whilst a brown oil remains in solution (p. 550).

White, inodorous and tasteless mass, melting at 59 to 60°, and solidifying at 58 to 59° to a shining mass of fine needles.

|  |  |  |  |  | Websky. mean. |
|---|---|---|---|---|---|
| 44 C | 264 | ........ | 78·11 | ........ | 77·89 |
| 42 H | 42 | ........ | 12·43 | ........ | 12·58 |
| 4 O | 32 | ........ | 9·46 | ........ | 9·53 |
| $C^{44}H^{42}O^4$ | 338 | ........ | 100·00 | ........ | 100·00 |

Isomeric with erucic acid, to which it bears the same relation that elaïdic acid bears to oleic acid (p. 74).

The acid becomes coloured and odorous at 120°. — Its soda-salt is obtained in the same way as that of erucic acid, and becomes coloured at 110°.

### *Appendix to Erucic Acid.*

**1. SINAPOLEIC ACID.**    Occurs in the seeds of black and white mustard. It is separated from an ethereal solution of the lead-salt by hydrochloric acid and alcohol, and is converted into a baryta-salt by Gottlieb's method (p. 63) (Darby, *Ann. Pharm.* 69, 6).

| *According to Darby.* | | | | *According to Städeler.* | | | | Darby. |
|---|---|---|---|---|---|---|---|---|
| 38 C | 228 | .... | 61·2 | 40 C | 240 | .... | 60·71 | .... 60·57 to 61·20 |
| 36 H | 36 | .... | 9·6 | 39 H | 39 | .... | 9·87 | .... 9·81 „ 9·76 |
| 4 O | 32 | .... | 8·8 | 5 O | 40 | .... | 10·06 | |
| BaO | 76·6 | .... | 20·4 | BaO | 76·6 | .... | 19·36 | .... 19·90 „ 20·4 |
| $C^{38}H^{36}BaO^5$ 372·6 .... 100·0 | | | | $C^{40}H^{37}BaO^4,2HO$ 395·6 .... 100·00 | | | | |

The percentage of baryta is not altered by repeated crystallisation. Städeler (*Ann. Pharm.* 87, 135) supposes the salt to contain either (in Darby's formula) 1 atom or (in his own formula) 2 atoms of water. The liquid acid of rape-oil may, according to Städeler, be sinapoleic acid.

**2. CRYSTALLINE FAT FROM OIL OF MUSTARD.** — The expressed oil of mustard (apparently of the white seed) is shaken up with cold alcohol of 36° B.; and the alcohol is decanted and evaporated to one-third, whereupon the fat crystallises on cooling. — It forms white, pearly, transparent laminæ and needles, melting at 120°, solidifying in a crystalline mass on cooling, and volatilising partially undecomposed. It is slowly converted by nitric acid (without formation of oxalic acid) into a yellow resin, which assumes a scarlet colour with potash. It is

not saponifiable by potash. Dissolves in cold alcohol and ether, and more freely in the hot liquids (Henry & Garot, *J. Chim. méd.* 1, 469 ; *Berz. Jahresber.* 6, 242 and 243). This fat appears to be cholesterin (Kr.). Darby found the soaps of the fatty oils of white mustard quite soluble in water, which is contrary to the statements of Henry & Garot. — The latter chemists, by exhausting with ether the sulpho-cyanate of sinapine (xiv, 528) which crystallises from the above extract on further evaporation, obtained a red fat of mustard, the vapour of which reddened paper held over it. The oil dissolves in alcohol, forms a cochineal-red solution with ether, and does not redden ferric salts.

3. SIMON'S SINAPISINE. — Different from the sinapisine of Boutron and Frémy (xiv, 524). — Obtained only from black mustard. — Flour of mustard is repeatedly exhausted with alcohol of 94 p. c. until the residue is quite free from harshness ; the residue is pressed ; and the liquid is filtered and distilled to remove the greater part of the alcohol. The residual liquid is then shaken with four times its bulk of ether : the ether is poured off ; and this operation is repeated at least five times. The extract remaining on distilling off the ether is again treated with small quantities of ether, which leaves sugar, fat oil (?), and soft resin undissolved ; the ethereal solution is evaporated, and the residue taken up afresh with a small quantity of ether. This last proceeding is repeated until the residue is completely soluble in ether, whereupon the residue is dissolved in alcohol of 90 p. c., which leaves fatty oil undissolved ; the solution is decolorised with animal charcoal ; and the filtrate is evaporated. A portion of the sinapisine now crystallises out, while another portion crystallises only after the spontaneously evaporated mother-liquor is treated afresh with alcohol, and the fatty oil still present is removed. The product is purified by recrystallisation from ether and alcohol. Fifty-five pounds of mustard yield 80 grains of sinapisine. — Dazzling-white crystals, having the appearance of fish-scales. Less easily fusible than the fat and susceptible of sublimation. Free from sulphur. — Insoluble in acids and in alkalis, and does not colour them yellow. Dissolves with moderate facility in alcohol, very easily in ether, and in oils both fat and volatile (Simon, *Pogg.* 43, 651 ; 50, 379).

4. FATTY OIL OF BLACK MUSTARD. — From *Sinapis nigra.* Golden-yellow or brown-yellow oil of sp. gr. 0·902 (Fontenelle), 0·917 at 15° (Schübler) ; thicker than olive-oil (Fontenelle), thinner than olive-oil and rape-oils, becoming thick at — 12° to — 15°, and solidifying to a brownish-yellow mass at — 17·5° (Schübler, *Br. Arch.* 14, 99). The cold-pressed oil has a faint odour of mustard, and a mild taste ; when hot-pressed it is acrid. — It does not easily turn rancid. With mercurous nitrate it assumes an orange-yellow colour, without solidifying. It forms a yellow, very hard soda-soap. Dissolves in 1000 parts (Fontenelle, *J. Chim. méd.* 1, 131 ; *Berz. Jahresber.* 6, 263), 1200 parts (Thibierge, *N. Tr.* 4, 2, 259) of alcohol of sp. gr. 0·833, and in 4 parts of ether. — Contains the glycerides of erucic acid, of a peculiar oleic acid, and of stearic acid (Darby).

5. FATTY OIL OF WHITE MUSTARD. — From *Sinapis alba.* Limpid, amber-yellow, inodorous oil, of sp. gr. 0·9142 at 15° (Schübler), 0·9153 (van Kerckhoff). Tastes mild (Darby) ; somewhat acrid (Schübler). Does

not solidify in the cold of winter, but becomes thick and turbid (Darby). It thickens at $-11°$ to $-15°$, and solidifies at $-16°$ to a yellowish-white butter (Schübler). Contains sulphocyanate of sinapine (xiv, 528), which it gives up to strong alcohol (Henry & Garot). Contains the glycerides of erucic acid, and of a peculiar oleic acid (Darby, *Ann. Pharm.* 69, 1).

6. BRASSICA-OILS. — From the seeds of various species of *Brassica* (Handbuch, viii [2], 38. The following have been distinguished :—

a. *Oil of Winter Rape.* (*Winterrepsöl. Winterrübsenöl.*) — From *Brassica Napus oleïfera*, Dec. Brownish-yellow; of sp. gr. 0·902 (Brandis), 0·915 at $15°$ (Lefebvre), 0·9182 at $11°$ (Scharling), 0·9193 (Brisson), 0·9128 at $15°$; of the commercial hot-pressed oil 0·917 (Schübler). Deposits tallow at $-1°$, and solidifies completely to a yellowish-white butter at $-4°$ (Schübler). The freshly expressed oil deposits mucus on standing, becoming clear, and appearing greenish-yellow in the upper, golden-yellow in the lower layers. When heated to $200°$ it acquires a greenish-yellow colour and a stronger odour, and at $350°$ undergoes decomposition, giving off vapours which condense to an acid, limpid, yellowish-green oil, having a strong odour. At $0°$ it solidifies in 6 or 8 hours to a butter, which melts slowly at $5°$ to $6°$. It contains the glycerides of erucic acid and a peculiar fluid oleic acid, which does not yield sebacic acid on distillation. It dissolves slightly in alcohol, easily in ether (Websky).

b. *Colza-oil.* (*Kohlrepsöl. Kohlsaatöl. Huile de Colza.*) — From *Brassica compestris oleïfera*, Dec. Brownish-yellow, nearly inodorous and tasteless oil, having, when expressed hot or when long kept, a disagreeable after-taste (Schübler). Sp. gr. 0·9136 (Schübler), 0·9143 (van Kerckhoff), 0·915 at $15°$ (Lefebvre). It is the least limpid of the brassica-oils. It deposits a little tallow at $-4°$, and solidifies to a yellow butter at $-6°$ (Schübler). — The yellow cold-pressed oil contains, on the average, 70·32 p. c. C., 10·58 H., and 19·10 O.; it forms with chlorine a yellow, very viscid compound of sp. gr. 1·060 at $10°$, containing 17·68 p. c. of chlorine, and with bromine a similar compound of sp. gr. 1·253 at $21·5°$, containing 32·5 p. c. of bromine. These bodies are represented by the formulæ $C^{20}ClH^{17}O^4$ and $C^{20}BrH^{17}O^4$ (Lefort, *N. J. Pharm.* 23, 284). — With alcoholic ammonia it yields a small quantity of amide, solidifying at $82°$ (Carlet).

c. *Oil of Summer Rape.* (*Sommerrepsöl. Sommerrübsenöl.*) — From *Brassica præcox*, Dec. Brownish-yellow, viscid oil, of sp. gr. 0·9139 (Schübler), 0·9171 (van Kerckhoff), 0·9157 at $15°$ (Lefebvre), 0·9223 at $11°$ (Scharling). It deposits tallow at $-8°$ only, and solidifies to a yellow-white butter at $-10°$ (Schübler).

d. *Oil of Turnip-stemmed Cabbage* (*Kohlrübenöl. Huile de navette.*) — From *Brassica Napobrassica*, Mill. Resembles winter rape-oil. Sp. gr. 0·9141 at $15°$ (Schübler), 0·9179 at $11°$ (Scharling). Viscid: deposits tallow below $0°$, and solidifies to a yellowish-white butter at $-4°$ (Schübler).

e. *Turnip oil.* (*Wasserrepsöl. Wasserrübenöl.*) — From *Brassica Rapa.* Brownish-yellow oil, the thinnest of the brassica-oils; has a sp. gr. of 0·9167 at $15°$. Deposits tallow at $-4°$ to $-6°$, and solidifies to a

whitish-yellow butter at − 7·5°. Remains greasy when exposed to the air (Schübler). Braconnot resolved this oil (or a ?) by pressure, at − 4°, into 54 parts of yellow oil, not solidifiable in the cold, and 46 parts of tallow melting at 7·5°, and yielding, when treated with sulphuric or nitric acid, a tough elastic mass, but no stearic or oleic acid. —It yields soaps inferior to those made with olive-oil or animal fats (Pelletier).

On the adulteration of rape-oil, see Laurol (*N. J. Pharm.* 2, 397 ; *J. pr. Chem.* 28, 251); Gobley (*N. J. Pharm.* 4, 285). — Rape-oil yields by distillation with water an acid distillate, having an odour of radishes, upon which floats an oily layer having a burning taste. The same products are obtained by distillation with aqueous potash (Glaser, *Repert.* 22, 102). — By the dry distillation of rape-oil, a mixture of acrolein [sebacic acid (Scharling, *J. pr. Chem.* 43, 264)], fatty acids, and hydrocarbons is obtained, the latter of which, when passed over heated soda-lime, yield butyric and valerianic acids, and when oxidised with nitric acid, a brown-red, oily nitro-compound, and a mixture of fatty acids, including acetic, propionic, butyric, valerianic, caproic, and œnanthylic acids (Schneider, *Ann. Pharm.* 70, 107). — See also Reichenbach (*J. pr. Chem.* 1, 377) on the dry distillation of rape-oil. — Fresh rape-oil, boiled with oxide of lead and water, yields lead-plaster and neutral glycerin ; but oil which has become thick from exposure to the air, yields, besides lead-plaster, a liquid which, after removing the lead by means of hydrosulphuric acid, has an acid reaction, and reduces nitrate of silver, probably owing to the presence of acrylic acid (Ludwig, *Apoth. Ver. Zeit.* 1, 181).

Rape-oil distilled with excess of alkali emits an odour of amylic butyrate (Al. Müller, *Handwörterb.* 6, 874). — It takes fire with chlorate of potash and oil of vitriol (A. Vogel). — In contact with *mercurous nitrate* it is converted into a dark brown thick honey in the course of two or three days (Davidson). — Rape-oil assumes a green colour with oil of vitriol (Heidenreich ; van Kerckhoff, *Kopp's Jahresber.* 1859, 701). — 15 grammes of the oil mixed with 5 grammes of oil of vitriol becomes heated by 55°, and with 7½ grammes of sulphuric acid containing 90 p. c. of oil of vitriol, by 37·5° (Fehling). — Pale rape-oil (a ?) agitated with ¼th of its volume of sulphuric acid of sp. gr. 1·475 remains uncoloured after 15 minutes, but with acid of sp. gr. 1·53 it acquires a faint red, and with acid of sp. gr. 1·635 a brown colour. It is not coloured by similar treatment with syrupy phosphoric acid, or with nitric acid of sp. gr. 1·33 or weaker. A mixture of nitric and sulphuric acids colours it dark-brown in two minutes. When heated to boiling with ⅕th of its volume of caustic soda of sp. gr. 1·34, it yields a solid dirty-white mass (Calvert, *J. pr. Chem.* 61, 354). — All the brassica oils blacken silver vessels in which they are boiled with excess of alkali, even when mixed with linseed or nut-oil, owing to the presence of sulphur (Mailho, *Compt. rend.* 40, 1218; *Kopp's Jahresber.* 1855, 822).

f. *Oil of Chinese radish.* From the seeds of *Raphanus Chinensis,* Miller. Brownish-yellow oil, having a mild odour and taste, of sp. gr. 0·9187 at 15°. Thickens at − 10°, and soldifies to a white mass at − 16° (Schübler).

*Oxygen-nucleus* $C^{44}H^{32}O^{10}$.

# Colocytheïn.

$$? \ C^{44}H^{32}O^{12} \ = \ C^{44}H^{32}O^{10}, O^{2}.$$
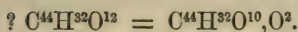
The colocynthin of Walz breaks up, when boiled with dilute sulphuric acid, into sugar and colocyntheïn, the latter of which separates in the form of a resin, and may be purified by dissolving it in absolute ether. It contains at 100°, on the average, 65·99 p. c. C., 8·62 H., and 25·99 O., from which numbers Walz calculates the formula $C^{44}H^{32}O^{13}$ (66 p. c. C., 8 H.). If colocyntheïn is to be regarded as an independent body, the formula $C^{44}H^{33}O^{13} = C^{44}H^{32}O^{12}, HO$ may perhaps be substituted for that just given (Kr.).

*Glucoside of Colocyntheïn.*

# Colocynthin.

HERBERGER.    *Repert.* 34, 368.

LEBOURDAIS.    *N. Ann. Chim. Phys.* 24, 58 ; *Pharm. Centr.* 1848, 763.

BASTICK.    *Pharm. J. Trans.* 10, 239 ; *N. J. Pharm.* 19, 346 ; abstr. *Kopp's Jahresber.* 1850, 550.

WALZ.    *N. Jahrb. Pharm.* 9, 16, and 225 ; *Pharm. Viertelj.* 7, 558 ; *N. Br. Arch.* 96, 141. — *N. Jahrb. Pharm.* 16, 10.

Braconnot (*J. Phys.* 84, 338) and Meissner (*N. Tr.* 2, 1, 27), previously attempted to prepare the bitter principle of colocynth. — Occurs principally in the pulp, and to a less extent in the pips of bitter apple (Walz).

*Preparation.* 1. Extract of colocynth, prepared with alcohol of sp. gr. 0·84 and thoroughly dried, is treated with cold water, and the liquid is filtered, colocynthitin then remaining in the residue. The aqueous liquid is precipitated with neutral acetate of lead, the precipitate is removed, and the filtrate is precipitated with the basic acetate. After separating the last precipitate, the liquid is freed from lead by hydrosulphuric acid, and precipitated with aqueous tannic acid not in excess ; the liquid is warmed, together with the precipitate, till the latter melts to a resin, which is then washed, dissolved in alcohol, and decomposed by agitating the solution with basic acetate of lead, or by digesting it with hydrated oxide of lead. The liquid, filtered from tannate of lead, freed from lead by hydrosulphuric acid, and decolorised with animal charcoal, leaves, on spontaneous evaporation, golden-yellow colocynthin, which is to be triturated and digested with anhydrous ether, whereupon pure colocynthin remains behind (Walz). — In this process a loss of colocynthin is incurred ; (*a*) in the colocynth exhausted with alcohol, from which it may be obtained by exhausting the colocynth with water, precipitating the extract with alcohol, evaporating the filtrate, and treating the residue in the same way as the alcoholic extract ; (*b*) in the precipitates thrown down by the neutral and basic acetates of lead, which precipitate it together with

colocynthitin, resin, and colouring matter (for the method of recovering it from these precipitates see *N. Jahrb. Pharm.* 9, 226); (*c*) in the liquid precipitated by tannic acid. The liquid is evaporated to one-half, neutralised with soda, and precipitated with tannic acid (!), and the precipitate is treated as above. The filtrate now obtained still contains colocynthin, which may be recovered by precipitating it with basic acetate of lead, neutralising the filtrate with caustic soda, precipitating with tannic acid, and decomposing the precipitate as above. Four and a-half pounds of colocynth yield 10 drachms of colocynthin (Walz).

2. Colocynth is macerated in water for two days and pressed; the press-cake is treated with a little cold alcohol of 20° B.; and the residue is exhausted with a large quantity of warm, not boiling, alcohol of 38° B. The latter tincture is evaporated to an extract, which is freed from fat by ether, and dissolved in a large quantity of water; the solution is filtered and precipitated with neutral acetate of lead; and the filtrate is freed from lead by hydrosulphuric acid, evaporated to a syrup, and mixed with a slight excess of ammonia. The yellow flocks thereby precipitated are dissolved in alcohol and decolorised with animal charcoal, and the filtrate is evaporated to dryness (Herberger). — In this way the greater part of the colocynth is left in solution (Walz). — Bastick precipitates with neutral acetate of lead the extract prepared with cold water and heated to boiling; filters after cooling; frees the filtrate from lead by sulphuric acid, and from acetic acid by boiling; and evaporates to dryness. From the residue strong alcohol takes up colocynthin, which remains, on evaporation, as a neutral reddish-brown resin. — Colocynthin thus prepared is not completely soluble in water (Walz). — Lebourdais precipitates a concentrated infusion of colocynth with neutral acetate of lead, and allows the filtrate to run slowly through a funnel containing animal charcoal; then washes the charcoal, which has taken up colocynthin, with water, dries it, and boils it with alcohol, which leaves small nodules when evaporated. — The whole of the colocynthin is precipitated by charcoal only after long standing (Walz).

*Properties.* Amorphous yellow mass, which is said to crystallise in whitish-yellow tufts when the alcoholic solution is slowly evaporated (Walz).

|  | | | | Walz. mean at 100°. |
|---|---|---|---|---|
| *Calculation according to Walz.* | | | | |
| 56 C | 336 | ............ | 59·78 | 59·41 |
| 42 H | 42 | ............ | 7·47 | 7·64 |
| 23 O | 184 | ............ | 32·75 | 32·95 |
| $C^{56}H^{42}O^{23}$ | 562 | ............ | 100·00 | 100·00 |

*Decompositions.* 1. Colocynthin, when heated, *burns* without leaving a residue. — 2. It forms with *oil of vitriol* a deep red solution, which afterwards turns brown, and is rendered turbid by water (Walz). Bastick's colocynthin is carbonised by oil of vitriol. — 3. It dissolves in *nitric acid* of sp. gr. 1·45, with abundant evolution of red fumes, and forms a yellow amorphous acid, precipitable by water (Bastick). According to Walz it dissolves in nitric acid of sp. gr. 1·52, apparently unaltered. — 4. By mixing its aqueous solution with *dilute sulphuric* or *hydrochloric acid,* and more completely by long boiling therewith, it is resolved into

colocynthein and sugar, 13 parts of colocynthin yielding a quantity of sugar, which reduces an amount of alkaline solution of cupric oxide corresponding to 1 part of grape-sugar:

$$C^{36}H^{42}O^{23} + 2HO = C^{44}H^{32}O^{15} + C^{12}H^{12}O^{12} \text{ (Walz)}.$$
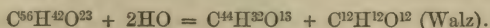
5. *Bromine-water* precipitates aqueous colocynthin and decolorises it. Colocynthin reduces *terchloride of gold* in 24 hours (Walz).

Colocynthin dissolves in 8 parts of *water* at 12°, and in 6 parts of boiling water, and is deposited from the solution in the form of an oil on cooling. The aqueous solution does not precipitate metallic salts, and renders ferrous sulphate only slightly cloudy.—It dissolves in 6 parts of weak, and in 10 parts of absolute *alcohol*, and is precipitated from the solution by ether, in which it is not soluble. — It is precipitated from its aqueous solution by *tannic acid* (Walz).

*Resin of Colocynth.* — When an alcoholic extract of colocynth is freed from fat by ether, and from bitter substance by water, the resin remains as a yellowish-brown, brittle, inodorous, very bitter mass, which melts when heated, dissolves with yellow colour in hot nitric acid, and colours oil of vitriol dark brown. It dissolves in warm aqueous ammonia and potash to a yellowish-brown liquid, precipitable in yellow flocks by acids; and is easily soluble in alcohol, but insoluble in ether and in fatty and volatile oils (Meissner). The resin dissolves for the most part in aqueous carbonate of soda, throwing down yellowish-grey flocks, and is soluble to a great extent in warm aqueous oxalic acid, forming a solution, from which it is thrown down as a yellow-white precipitate by tannic acid.

*Colocynthitin.* — To prepare this substance, the portion of alcoholic extract of colocynth which is insoluble in water is exhausted with ether; the brown solution is decolorised with animal charcoal; the filtrate is evaporated; and the dry residue is washed with absolute alcohol. The undissolved portion, dissolved in boiling alcohol, and decolorised with animal charcoal, yields crystals of colocynthitin on cooling, whilst the remainder of the solution solidifies to a jelly, which is slowly transformed into a crystalline powder of colocynthitin. — Tasteless crystalline powder, consisting of microscopic oblique rhombic prisms. Contains at 100°, on the average, 69·8 p. c. C., 9·4 H., and 20·8 O. It is soluble in boiling, but insoluble in cold absolute alcohol (Walz).

*Primary Nucleus $C^{44}H^{44}$.*

## Benic Acid.

$$C^{44}H^{44}O^4 = C^{44}H^{44},O^4.$$

MULDER & A. VÖLCKER. *Scheik. Onderz.* 3 Th. 5 St. 545; *J. pr. Chem.* 39, 351: abstr. *Ann. Pharm.* 64, 342.

Respecting Walter's benic acid, see xvi, 365.

*Source.* In oil of ben (xvi. 386) from *Moringa oleïfera.*

*Preparation.* The fatty acids obtained by saponifying the oil and decomposing the soap, are separated by pressure into a fluid and a solid portion, the latter of which is crystallised from alcohol to separate the more easily fusible margaric acid from the less easily fusible fatty acids. There remains undissolved, in too small quantity for further examination, an acid, which melts at 83°, dissolves in stronger alcohol, and contains 81·5 p. c. C., and 13·86 H.

*Properties.* Benic acid solidifies from fusion in white friable needles, resembling stearic acid. It melts at 76°:

|  |  |  |  |  | Völcker. mean. |
|---|---|---|---|---|---|
| 44 C | 264 | ........ | 77·65 | ........ | 77·53 |
| 44 H | 44 | ........ | 12·94 | ........ | 12·90 |
| 4 O | 32 | ........ | 9·41 | ........ | 9·57 |
| $C^{44}H^{44}O^4$ | 340 | ........ | 100·00 | ........ | 100·00 |

The above is Strecker's formula (*Ann. Pharm.* 64, 346). Mulder gives the formula $C^{42}H^{42}O^4$. — The acid melting at 83° may have the formula $C^{96}H^{96}O^4$ (81·8 p. c. C., 13·4 H.) but on account of its too low melting-point (as compared with melissic acid), Heintz regards it as a mixture, which may also be the case with benic acid.

*Soda-salt.* — A hot alcoholic solution of the salt solidifies to a jelly, which becomes crystalline when diluted with alcohol, but not on long standing only.

|  |  |  |  |  | Völcker. mean. |
|---|---|---|---|---|---|
| 44 C | 264 | ........ | 72·92 | ...... | 72·03 |
| 43 H | 43 | ........ | 11·88 | ........ | 11·78 |
| 3 O | 24 | ........ | 6·63 | ........ | 7·55 |
| $NaO^4$ | 31 | ........ | 8·57 | ........ | 8·64 |
| $C^{44}H^{43}NaO^4$ | 362 | ........ | 100·00 | ........ | 100·00 |

*Baryta-salt.* — Chloride of barium throws down from the alcoholic soda-salt a precipitate resembling stearate of baryta.

|  |  |  |  |  | Völcker. |
|---|---|---|---|---|---|
| 44 C | 264 | ........ | 64·78 | ........ | 64·74 |
| 43 H | 43 | ........ | 10·55 | ........ | 10·45 |
| 3 O | 24 | ........ | 5·89 | ........ | 6·10 |
| BaO | 76·5 | ........ | 18·78 | ........ | 18·71 |
| $C^{44}H^{43}BaO^4$ | 407·5 | ........ | 100·00 | ........ | 100·00 |

*Lead-salt.* — Precipitated from the soda-salt by neutral acetate of lead.

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 44 C | 264 | ........ | 59·59 | ........ | 58·43 |
| 43 H | 43 | ........ | 9·70 | ........ | 9·50 |
| 3 O | 24 | ........ | 5·42 | ........ | 6·06 |
| PbO | 112 | ........ | 25·29 | ........ | 26·01 |
| $C^{44}H^{43}PbO^4$ | 443 | ........ | 100·00 | ........ | 100·00 |

## Benate of Ethyl.

$$C^{48}H^{48}O^4 = C^4H^5O,C^{44}H^{43}O^3.$$
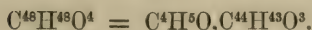
VÖLCKER.    *J. pr. Chem.* 39, 356.

On passing hydrochloric acid gas into an alcoholic solution of benic acid, the ether is deposited in crystals before the liquid becomes saturated with the gas.

Colourless, translucent, crystalline body, melting at 48° to 49°. Inodorous.

| | | | | | | Völcker. |
|---|---|---|---|---|---|---|
| 48 C | 288 | ........ | 78·26 | ........ | 78·48 |
| 48 H | 48 | ........ | 13·04 | ........ | 12·98 |
| 4 O | 32 | ........ | 8·70 | ........ | 8·54 |
| $C^4H^5O,C^{44}H^{43}O^3$ ........ | 368 | ........ | 100·00 | ........ | 100·00 |

*Bromine-nucleus*  C⁴⁴Br²H⁴².

## Bromerucic Acid.

$$C^{44}Br^2H^{42}O^4 = C^{44}Br^2H^{42},O^4.$$

R. OTTO.    *Zeitschr. f. Chem.* 8, 275 ; *Ann. Pharm.* 135, 226.

*Formation and Preparation.* Erucic acid is covered with water, and bromine is dropped into the liquid so long as the colour disappears on brisk agitation. The bromine is absorbed by the acid without liberation of hydrobromic acid. After pouring off the water and evaporating the excess of bromine in the air, the bromerucic acid formed is dissolved in warm alcohol, and crystallised from the cooled solution in small white nodules, melting at 42° to 43°.

| | | | | | Otto. mean. |
|---|---|---|---|---|---|
| | *Nodules.* | | | | |
| 44 C | 264 | ........ | 53·01 | ........ | 53·15 |
| 2 Br | 160 | ........ | 32·13 | ........ | 31·80 |
| 42 H | 42 | ........ | 8·43 | ........ | 8·80 |
| 4 O | 32 | ........ | 6·43 | ........ | 6·25 |
| $C^{44}Br^2H^{42}O^4$ .... | 498 | ........ | 100·00 | ........ | 100·00 |

Bromerucic acid does not decompose when kept. — It is converted into erucic acid by the action of *sodium-amalgam* on treating its alcoholic solution acidulated with hydrochloric acid.

*Baryta-salt.* — Thrown down as a white precipitate from the alcoholic ammonia-salt by acetate of baryta. Melts at 100°, and decomposes at that temperature, or on exposure to the air, taking up oxygen and becoming greasy.

| | *In vacuo.* | | | Otto. | | |
|---|---|---|---|---|---|---|
| $C^{44}Br^2H^{41}O^4$ ............ | 497 | ........ | 87·89 | | | |
| Ba.................... | 68·5 | ........ | 12·11 | ........ | 11·80 | |

| $C^{44}Br^2H^{41}BaO^4$ ........ | 565·5 | ........ | 100·00 | |
|---|---|---|---|---|

*Lead-salt.* — Plaster-like precipitate, separating from its solution in a large quantity of boiling absolute alcohol in small white crystals, which quickly turn rancid in the air.

| | *Crystals.* | | | Otto. | |
|---|---|---|---|---|---|
| $C^{44}Br^2H^{41}O^4$ ........ | 497 | ........ | 82·7 | | |
| Pb ................ | 104 | ........ | 17·3 | ........ | 16·6 |

| $C^{44}Br^2H^{41}PbO^4$ .... | 601 | ........ | 100·0 | |
|---|---|---|---|---|

The acid dissolves in *alcohol* and *ether*, and is precipitated from the solution in the form of an oil by water.

---

# COMPOUNDS CONTAINING 46 ATOMS OF CARBON.

*Primary Nucleus* $C^{46}H^{22}$; *Azo-nucleus* $C^{46}N^4H^{18}$.

## Aribine.

$$C^{46}N^4H^{20} = C^{46}N^4H^{18}, H^2.$$
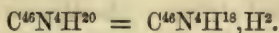
RIETH (& WÖHLER). *Göttinger Nachrichten* 1861, 201; *Ann. Pharm.* 120, 247; *N. Ann. Chim. Phys.* 64, 485; *Rép. Chim. pure* 4, 237; *Kopp's Jahresber.* 1861, 532; complete: *Dissertation über das Aribine*, von R. RIETH, Göttingen, 1861; abstr. *Chem. Centr.* 1861, 903.

In the bark of *Arariba rubra*, a Brazilian tree.

*Preparation.* The bark is exhausted by digestion with hot water containing sulphuric acid; the extract is concentrated, separated from deposited sulphate of lime, nearly neutralised with carbonate of soda, and precipitated with neutral acetate of lead. After removing the precipitate by filtration, the filtrate is treated with hydrosulphuric acid to free it from lead and colouring matter remaining in solution, and afterwards precipitated with carbonate of soda, and shaken repeatedly with ether, which takes up aribine. The ethereal solution is mixed with hydrochloric acid, and the hydrochlorate of aribine thereby precipitated is collected, and purified by crystallisation and washing with strong hydrochloric acid, after which its aqueous solution is decomposed by agitation with carbonate of soda and ether. The aribine purified by this process, repeated several times, is lastly crystallised from ether. It may be obtained in anhydrous and in hydrated crystals.

*Properties.* Colourless, highly lustrous, rhombic pyramids, or

prisms with angles of 76° 30′ and 103° 30′. Melts at 229°, and solidifies in a crystalline mass. When cautiously heated, it sublimes below the melting point in very delicate long needles, but when it is rapidly heated, empyreumatic products are also formed. It has an alkaline reaction. Without action on polarised light.

| | | | | | | Rieth. *mean.* |
|---|---|---|---|---|---|---|
| 46 C | ............... | 276 | ......... | 78·43 | ......... | 78·33 |
| 4 N | ............... | 56 | ......... | 15·89 | ......... | 15·87 |
| 20 H | ............... | 20 | ......... | 5·68 | ......... | 5·79 |
| $C^{46}N^4H^{20}$ | ......... | 352 | ......... | 100·00 | ......... | 99·99 |

When aribine is heated with *iodide of ethyl* in a water-bath for a few days, yellow crystals are produced, which are soluble in water, contain 49·29 p. c. C., and 4·62 H., and are probably formed by the combination of 2 atoms of ethylic iodide with 1 atom of aribine:

$$C^{46}N^4H^{20} + 2C^4H^5I = C^{46}N^4H^{18}(2C^4H^5),2HI$$
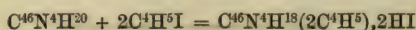
(calc. 48·82 p. c. C., 4·52 H.). — When an alcoholic solution of these crystals is decomposed with oxide of silver and the solution is evaporated (after removing the iodide of silver) *hydrate of biethylaribine* remains as an amorphous, coloured varnish, which forms a crystalline compound with hydrochloric acid. Alcoholic biethylaribine again heated with iodide of ethyl yields a brown liquid, or when evaporated, a black crystalline mass, with a large quantity of free iodine.

*Combinations. With Water.* A. *Hydrated Aribine.* — Flat, four-sided prisms, with oblique end-faces, hollow throughout the entire length, and open above. The crystals, which are transparent and shining, effloresce in the air, becoming white and opaque, and lose the whole of their water of crystallisation at 100°.

| | *Crystals.* | | | | | Rieth. *mean.* |
|---|---|---|---|---|---|---|
| $C^{46}N^4H^{20}$ | ..................... | 352 | ......... | 70·97 | ......... | 71·59 |
| 16 HO | ..................... | 144 | ......... | 29·03 | ......... | 28·41 |
| $C^{46}N^4H^{20}$ + 16aq | .... | 496 | ......... | 100·00 | ......... | 100·00 |

B. *Aqueous solution.* — Aribine dissolves in 7762 parts of water at 23°, and more freely in hot water. It is deposited from a hot saturated solution, at first in anhydrous and afterwards in delicate feathery hydrated crystals.

C. *Iodine, bromine,* and *chlorine* throw down from dilute hydrochlorate of aribine, brown, yellow, or colourless crystalline needles, which dissolve on warming the liquid, and appear again on cooling.

D. Aribine combines with *acids* to form salts which are generally easily crystallisable, and contain 2 or 4 atoms of acid to 1 atom of base. From a dilute aqueous solution of the hydrochlorate, caustic soda and its carbonate, ammonia, and lime-water throw down crystalline aribine, which dissolves when the liquid is warmed, and makes its appearance again as it cools. Baryta- and strontia-water throw down insoluble precipitates on warming. Many salts and acids, including

the following, likewise produce crystalline precipitates [owing, perhaps, to the fact, that hydrochlorate of aribine is insoluble in saline solutions, as well as in strong hydrochloric acid (Kr.)]: phosphoric acid, arsenic acid, arsenate of ammonia, iodide and bromide of potassium, bromate, chlorate, nitrite, and nitrate of potash, phosphate of soda, chloride of barium, sulphide of barium, sulphide of strontium, chromate and bichromate of potash, mercuric chloride, cyanide of potassium, ferrocyanide and ferricyanide of potassium, cyanate and sulphocyanate of potash, acetate of soda, and acetate of magnesia. The following salts do not produce precipitates; acetate, oxalate, and binoxalate of ammonia, oxalate of potash, succinate of ammonia, and acid tartrate of soda. Acetate of ammonia dissolves the precipitate produced by acetate of soda, and tartaric acid that formed by neutral tartrate of soda.

*Sulphate of Aribine.* — A. *Bi-acid.* — Formed from hydrochlorate of aribine and sulphate of silver.

|  |  | at 120°. |  |  | Rieth. |
|---|---|---|---|---|---|
| $C^{46}N^4H^{20}$ | ............... | 352 | ........ | 78·23 |  |
| $2(HO,SO^3)$ | ............... | 98 | ........ | 21·77 | ........ 21·41 |
| $C^{46}N^4H^{20},2(HO,SO^3)$ | .... | 450 | ........ | 100·00 |  |

B. *Quadri-acid.* — Formed by mixing aribine with excess of sulphuric acid and washing the resulting salt, which is insoluble in the excess of acid, with ether and ether-alcohol:

|  |  |  |  |  | Rieth. |
|---|---|---|---|---|---|
| $C^{46}N^4H^{20}$ | ............... | 352 | ........ | 64·24 |  |
| $4(HO,SO^3)$ | ............... | 196 | ........ | 35·76 | ........ 35·36 |
| $C^{46}N^4H^{20},4(HO,SO^3)$ | .... | 548 | ........ | 100·00 |  |

*Hydrochlorate of Aribine.* — Formed by passing dry hydrochloric acid gas over aribine, and expelling the excess of acid by a current of dry air at 100°. — Slender needles, easily soluble in water and precipitable from the solution by strong hydrochloric acid. The salt is soluble in fusel-oil, but quite insoluble in ether.

|  |  |  |  |  | Rieth. |
|---|---|---|---|---|---|
| $C^{46}N^4H^{20}$ | ............ | 352 | ........ | 82·83 |  |
| $2HCl$ | ............ | 73 | ........ | 17·17 | ........ 16·50 |
| $C^{46}N^4H^{20},2HCl$ | .... | 425 | ........ | 100·00 |  |

*Chloroplatinate of Aribine.* — Bichloride of platinum throws down from hydrochlorate of aribine, pale-yellow needles, which do not dissolve on warming, even after addition of hydrochloric acid.

|  |  |  |  |  | Rieth. |
|---|---|---|---|---|---|
| $C^{46}N^4H^{20},2HCl,4Cl$ | ........ | 567 | ........ | 74·18 |  |
| $2Pt$ | ............... | 197·4 | ........ | 25·82 | ........ 25·55 |
| $C^{46}N^4H^{20},2HCl,2PtCl^2$ | .... | 764·4 | ........ | 100·00 |  |

Aribine dissolves easily in cold, and more easily in hot *alcohol*, less freely in *ether*, and also in *fusel-oil*.

*Primary Nucleus* $C^{46}H^{30}$; *Oxygen-nucleus* $C^{46}H^{20}O^{10}$.

## Ononetin.

$$C^{46}H^{22}O^{12} = C^{46}H^{20}O^{10},H^2O^2.$$
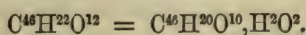
HLASIWETZ. *Wien. Acad. Ber.* 15, 152.

Formed, together with sugar, by boiling onospin with acids, or together with formic acid by boiling formonetin.

Onospin is heated with 10 parts of water, and dilute sulphuric acid is dropped into the solution till turbidity is produced and until the supernatant liquid deposits oily drops, and again becomes clear. The ononetin deposited on cooling is purified by crystallisation from alcohol. — Or, formonetin is boiled with baryta-water, carbonic acid is passed into the solution, and the precipitate is boiled with alcoholic sulphuric acid, which dissolves the ononetin.

*Properties.* Radiated groups of brittle needles, having a high re-fractive power. Melts at 120°, losing 1·86 p. c. in weight, and solidi-fying to a crystalline mass on cooling.

|  |  | at 100°. |  |  | Hlasiwetz. mean. |
|---|---|---|---|---|---|
| 46 C | 276 | ........ | 70·05 | ........ | 69·33 |
| 22 H | 22 | ........ | 5·58 | ........ | 5·72 |
| 12 O | 96 | ........ | 24·37 | ........ | 24·95 |
| C⁴⁶H²²O¹² | 394 | ........ | 100·00 | ........ | 100·00 |

The above is Limpricht's formula (*Lehrbuch*, 623): Hlasiwetz proposes $C^{48}H^{22}O^{13}$.

*Decompositions.* 1. Ononetin *heated* on platinum-foil evolves vapours which excite coughing, burns with flame, and leaves an easily com-bustible charcoal. — 2. *Oil of vitriol* and *peroxide of manganese* colour ononetin a fine carmine-red. — 3. Ononetin heated with *nitric acid*, melts to a resin, evolving vapours which excite tears, and forming oxalic acid, together with picric or styphnic acid. — 4. The ammonia-cal solution assumes a dark chrome-green colour in the air, and is afterwards precipitable by acids in dark-red resinous flocks.

Crystallised ononetin is nearly insoluble in *water;* when freshly precipitated by acids, it dissolves to a small extent in boiling water, from which it crystallises on cooling.

Ononetin dissolves easily in aqueous *alkalis.* It is precipitated from its alcoholic solution by *basic acetate of lead,* but not by other metallic salts. — It is coloured dark-red by *sesquichloride of iron.*

It dissolves easily in *alcohol,* and slightly in warm *ether.*

*Conjugated Compounds of Ononetin.*

### a. With Formic Acid.

## Formonetin.

$$C^{48}H^{20}O^{12} = C^{46}H^{19}O^9, C^2HO^3.$$
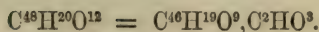
Hlasiwetz. *Wien. Acad. Ber.* 15, 160.

*Formation.* Ononin breaks up on boiling into formonetin and sugar.

*Preparation.* Ononin is boiled with dilute sulphuric or hydrochloric acid till the originally clear solution solidifies to a pulp of flocculent crystals, which are to be washed with cold water and crystallised from boiling alcohol. Or the crystalline mass is dissolved in ammonia, and the filtered solution is precipitated with so much hydrochloric acid that a portion of the formonetin still remains in solution, together with the whole of the colouring matter. The gelatinous precipitate thus obtained is collected, washed, and crystallised from alcohol.

*Properties.* Small tasteless crystals.

|  | at 100° |  |  |  | Hlasiwetz. mean. |
|---|---|---|---|---|---|
| 48 C ............... | 288 | ........ | 71·29 | ........ | 70·88 |
| 20 H ............... | 20 | ........ | 4·95 | ........ | 4·87 |
| 12 O ............... | 96 | ........ | 23·76 | ........ | 24·25 |
| $C^{48}H^{20}O^{12}$ ........ | 404 | ........ | 100·00 | ........ | 100·00 |

Hlasiwetz gives the formula $C^{50}H^{20}O^{13}$.

Formonetin assumes a fine violet colour with *oil of vitriol* and *oxide of manganese.* — The solution in aqueous *alkalis* or in *baryta-water* breaks up on boiling into ononetin and a formiate :

$$C^{48}H^{20}O^{12} + 4HO = C^{46}H^{22}O^{12} + C^2H^2O^4.$$
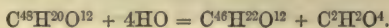
It is insoluble in water and is not acted on by aqueous *ammonia.* It is not precipitated by *sesquichloride of iron* or other *metallic salts.* It is soluble in boiling *alcohol*, but nearly insoluble in *ether.*

### b. With Sugar.

## Onospin.

$$C^{58}H^{34}O^{24} = C^{46}H^{22}O^{12}, C^{12}H^{12}O^{12}.$$
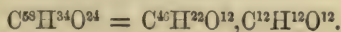
Hlasiwetz. *Wien. Acad. Ber.* 15, 147.

¶ *Formation.* Ononin, boiled with baryta-water, breaks up into onospin and formic acid.

*Preparation.* Ononin is boiled with baryta-water till a pure yellow precipitate is produced on the addition of more baryta-water; the liquid is cooled and treated with a current of carbonic acid, or mixed with sulphuric acid not in excess, so long as a brisk effervescence is produced; and the precipitate is separated by filtration, washed with a little cold water, removed from the filter while still moist, and after neutralisation with a few drops of dilute sulphuric acid, boiled repeatedly with water.  The hot filtered decoctions solidify on cooling to a crystalline mass of onospin, which is collected and recrystallised three or four times from hot water, at last together with animal charcoal.  The liquid, filtered from the carbonate of baryta and onospin, contains formiate of baryta and sometimes also onospin-baryta, which it deposits in the form of an amber-yellow resin on cooling.  An alcoholic solution of this body, when decomposed by excess of sulphuric acid and filtered, yields onospin on evaporation.

*Properties.* Microscopic crystals, drying up to a shining pellicle, which is slightly electric when rubbed.  Nearly tasteless.  Melts at 162° and does not undergo further alteration at 200°, or sublimes in small portion, and solidifies to a translucent, hygroscopic gum, which is highly electric when rubbed, has a bitterish styptic taste, and crystallises from boiling water.

|        |   | at 100°. |   |        |   | Hlasiwetz. mean. |
|--------|---|----------|---|--------|---|------------------|
| 58 C   |   | 348      |   | 60·63  |   | 60·15            |
| 34 H   |   | 34       |   | 5·92   |   | 6·04             |
| 24 O   |   | 192      |   | 33·45  |   | 33·81            |
| C⁵⁸H³⁴O²⁴ |   | 574   |   | 100·00 |   | 100·00           |

The above is Limpricht's formula.  Hlasiwetz proposed C⁶⁰H³⁴O²⁵.

*Decompositions.*  1. Onospin, when heated on platinum-foil, melts, *burns* with flame, and emits a faint odour of sugar. — 2. It dissolves in *oil of vitriol* with reddish-yellow colour, which changes to carmine-red on addition of *oxide of manganese.* — 3. It is oxidised by *nitric acid,* with formation of oxalic acid. — 4. When boiled with dilute *hydrochloric* or *sulphuric acid,* it dissolves and breaks up into sugar and ono-netin, which separates in crystals or in oily drops :

$$C^{58}H^{34}O^{24} = C^{46}H^{22}O^{12} + C^{12}H^{12}O^{12} \text{ (Limpricht).}$$
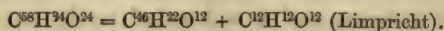
In this decomposition, 100 parts of onospin yield, on the average, 29·9 parts of sugar (calc. 31·36 p. c. C¹²H¹²O¹²).

*Combinations.*  Onospin dissolves in all proportions in boiling *water* and crystallises from the solution on cooling.

It dissolves easily in aqueous *ammonia* and in aqueous *alkalis,* from which it is precipitated by acids.  It crystallises unaltered from its solution in ammonia.

*Onospin-baryta.*  Occasionally obtained in the preparation of onospin as a resin containing variable proportions of baryta.  It dissolves easily in alcohol and crystallises from the solution after long standing.

Onospin is not precipitated by *metallic salts* with the exception of *basic acetate of lead.* It does not reduce a boiling solution of *nitrate of silver.* It colours *sesquichloride of iron* a dark cherry-red, even in dilute aqueous or alcoholic solution. It does not reduce an *alkaline solution of cupric oxide.*

It is easily soluble in *alcohol,* but nearly insoluble in *ether.*

### c. With Formic Acid and Sugar.

## Ononin.

$$C^{60}H^{34}O^{26} = C^{46}H^{21}O^{11},C^{12}H^{12}O^{12},C^2HO^3.$$
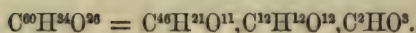
REINSCH. *Repert.* 76, 12 ; 78, 18 ; *Berzel. Jahresber.* 23, 506.
HLASIWETZ. *Wien. Acad. Ber.* 15, 142 ; *J. pr. Chem.* 65, 419 ; abstr. *Pharm. Centr.* 1855, 449 and 470 ; *Pharm. Viertelj.* 4, 544 ; *Chem. Gaz.* 1855, 321 and 342 ; *N. Ann. Chim. Phys.* 46, 374 ; *Kopp's Jahresber.* 1855, 713.

Discovered by Reinsch in the roots of *Ononis spinosa :* investigated principally by Hlasiwetz. — Different from ononide (p. 61).

*Preparation.* 1. When a decoction of the root is precipitated by neutral acetate of lead, and hydrosulphuric acid is passed into the filtrate, sulphide of lead is precipitated, and with it the ononin, which may be extracted from the washed and dried precipitate by three or four times repeated boiling with alcohol, and purified by recrystallisation from alcohol with the help of animal charcoal. The precipitate produced by neutral acetate of lead, when converted into sulphide of lead and boiled with alcohol, yields a little more ononin, but not sufficient to compensate for the alcohol and time employed (Hlasiwetz). — 2. An alcoholic extract of the root is washed with warm water, and the residue is boiled with alcohol with addition of oxide of lead, which takes up ononin, and when filtered and evaporated, leaves it in crystals, which are to be further purified. The aqueous solutions treated as in 1 yield a little more ononin (Trommsdorff). — 3. The root is boiled with alcohol and the decoction is filtered hot and concentrated to a syrup, which is then freed by successive treatment with water, ether, and alcohol of 60 p. c. from substances soluble in those liquids. The residue is a pale-brown powder, a solution of which in boiling alcohol yields crystals of ononin on cooling and evaporation. The crystals are to be washed with cold alcohol of 75 p. c., which takes up ononide, and recrystallised from boiling alcohol, with the help of animal charcoal (Reinsch).

*Properties.* Colourless four-sided needles or laminæ ; according to Hlasiwetz inodorous and tasteless, but according to Reinsch they have a sweetish after-taste. Melts at 235°, undergoing some change and losing 2·65 p. c. in weight, and solidifying in the crystalline state on cooling (Hlasiwetz).

|  | at 100°. |  |  |  | Hlasiwetz. mean. |
|---|---|---|---|---|---|
| 60 C ............... | 360 | ........ | 59·80 | ........ | 59·87 |
| 34 H ............ | 34 | ........ | 5·64 | ........ | 5·60 |
| 26 O ............... | 208 | ........ | 34·56 | ........ | 34·53 |
| C⁶⁰H³⁴O²⁶ .... | 602 | ........ | 100·00 | ........ | 100·00 |

The above is Limpricht's formula (*Grundriss*, 680, and *Lehrbuch*, 622), which as it contains an even number of atoms, and accounts for the products of decomposition of the substance, and likewise agrees sufficiently well with the analyses, is preferable to that of Hlasiwetz, C⁶²H³⁴O²⁷ (Kr.).

*Decompositions.* 1. Ononin heated on platinum foil melts and *burns* with flame (Hlasiwetz). — 2. When *heated* in a glass tube, it yields a sublimate and leaves a brown residue, which afterwards carbonises (Reinsch). — 3. It forms, with *oil of vitrol*, a reddish-yellow solution, which afterwards turns cherry-red, and on addition of oxide of manganese, a fine carmine-red. — 4. It is dissolved by *nitric acid*, with yellow colour, and is decomposed, with formation of oxalic acid (Hlasiwetz), a bitter substance, and a peculiar acid (Reinsch). — 5. Its solution in hot *hydrochloric* or dilute *sulphuric acid* breaks up on boiling into sugar and formonetin, the latter of which crystallises out (Hlasiwetz) :

$$C^{60}H^{34}O^{26} = C^{48}H^{20}O^{12} + C^{12}H^{12}O^{12} + 2HO.$$
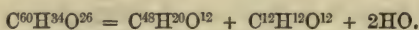
6. Ononin, subjected to prolonged boiling with *baryta*-water (or caustic potash), dissolves with yellow colour, emitting a faint aromatic odour and breaking up into onospin and formic acid (Hlasiwetz) :

$$C^{60}H^{34}O^{26} + 2HO = C^{58}H^{34}O^{24} + C^2H^2O^4.$$
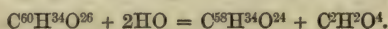
*Combinations.* Ononin is insoluble in cold, and but slightly soluble in boiling *water*, from which it crystallises on cooling. It is not affected by *chlorine-water*, or by *ammonia*, aqueous *sesquichloride of iron* or *metallic salts*. It is precipitated from its alcoholic solution in white flocks by *basic acetate of lead* (Hlasiwetz).

Ononin dissolves in strong *alcohol* on long boiling. After boiling for some time with water, it is taken up by moderately strong alcohol.

It is nearly insoluble in *ether* (Hlasiwetz ; Reinsch).

*Primary Nucleus* C⁴⁶H³⁴; *Oxyazo-nucleus* C⁴⁶N²H²⁴O⁸.

# Aricine.

$$C^{46}N^2H^{26}O^8 = C^{46}N^2H^{24}O^8,H^2.$$
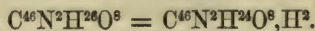
PELLETIER & CORIOL. *J. Pharm.* 15, 565 ; *N. Tr.* 21, 1, 127 ; *Repert.* 33, 364.

LEVERKÖHN. *Repert.* 33, 353.

PELLETIER. *Ann. Chim. Phys.* 51, 185 ; *Schw.* 67, 81 ; *Ann. Pharm.* 6, 23.

MANZINI. *N. J. Pharm.* 2, 95 ; abstr. *Compt. rend.* 15, 105 ; *J. pr. Chem.* 29, 42 ; *N. Br. Arch.* 32, 48 ; *N. Ann. Chim. Phys.* 6, 127. — *N. J. Pharm.* 2, 313.

F. L. WINCKLER. *Repert.* 75, 299 ; 81, 249

*Cusconine* (Pelletier ; Winckler). *Cinchovatine* (Manzini). — Discovered by Pelletier & Coriol in 1829.

Occurs in *China de Cusco vera* (Wiggers, 412), which was investi-
gated by Pelletier & Coriol and by Leverköhn as a spurious calisaya.
In *China Jaen palliaa* (Wiggers, 402) (Manzini). — Winckler examined
Pelletier's bark, which assumes a green colour with strong nitric acid,
as is the case also with the ethereal extract obtained from it.

*Formation.* Aricine is formed by treating kinone with nitrate of potash and
oil of vitriol, adding to the product water and zinc, and after 24 hours evaporating
and exhausting the residue with alcohol; the product is turned green by nitric acid
(Schoonbroodt, *Par. Soc. Bull.* 1, 107; *Chem. Centr.* 1863, 111). This statement
requires confirmation (Kr.).

*Preparation.* Aricine is obtained, in the same way as quinine, by
boiling the bark with acidulated water, treating the extract with lime,
and exhausting the lime-precipitate with alcohol of 36°. The alcoholic
extract is filtered hot and the brown filtrate is set aside for a day, when
it deposits the greater part of the aricine in fine crystals, which must
be removed. The mother-liquor is freed from most of the alcohol by
distillation; the black residue is treated with a slight excess of dilute
hydrochloric acid and mixed with a strong solution of chloride of
sodium, which precipitates the colouring matter; and the liquid is
filtered and precipitated by ammonia. The precipitate is redissolved
in hydrochloric acid, and the solution is precipitated by chloride of
sodium, filtered, and again precipitated by ammonia, until the aricine
appears of a straw-yellow colour, after which it is purified by crystalli-
sation from alcohol, with help of animal charcoal (Manzini). — Winckler
submits to distillation the tincture obtained by exhausting the lime
precipitate; dissolves the residual resin in very dilute acetic acid;
decolorises the solution with oxide of lead, basic acetate of lead, and
animal charcoal; precipitates with ammonia; and purifies the product
by crystallisation. In this way the bark yields about 1·4 p.c. of
aricine.

*Properties.* Thick needles, tasteless at first, afterwards warm and
acid, and having a very bitter taste when dissolved in acids (Pelletier
and Coriol). Very delicate prisms having a vitreous lustre, arranged
in circles (Winckler). According to Manzini, colourless crystals, longer
than those of cinchonine, inodorous, slowly exciting a bitter taste in the
mouth. Has an alkaline reaction. Does not undergo any alteration at
150° and melts at 188° without loss of weight, to a resin which has
the same melting-point when heated again (Manzini). Leverköhn's
aricine was bitter, not alkaline, and not crystallisable, but, like that of
the other chemists, it formed a tremulous jelly with sulphuric acid.

|  |  |  |  |  | Pelletier. |  | Manzini. mean at 120°. |
|---|---|---|---|---|---|---|---|
| 46 C | 276 | ........ | 70·05 | ........ | 69·6 | ........ | 69·59 |
| 2 N | 28 | ........ | 7·09 | ........ | 8·0 | ........ | 7·36 |
| 26 H | 26 | ........ | 6·60 | ........ | 7·0 | ........ | 7·04 |
| 8 O | 64 | ........ | 16·26 | ........ | 15·4 | ........ | 16·01 |
| $C^{46}N^2H^{26}O^8$ | 394 | ........ | 100·00 | ........ | 100·0 | ........ | 100·00 |

According to Pelletier, $C^{20}NH^{12}O^3$. Manzini's formula contains 1 at. of hydrogen
more than the one above given, which was preferred by Gerhardt (*Traité*, 4, 152).—
Isomeric with brucine.

Aricine gives off stinking empyreumatic products at 190°, leaving charcoal (Manzini). — It dissolves in strong *nitric acid* with dark-green colour, and in dilute acid with paler colour (Pelletier & Coriol). Winckler's aricine exhibits this coloration only when impure.

Aricine is nearly insoluble in *water*, but easily soluble in dilute *acids*, forming for the most part crystallisable salts, which dissolve even in weak warm alcohol. The salts are precipitated by caustic alkalis and their carbonates (Manzini). The precipitate is pulverulent, not resinous (Winckler). The salts are precipitated by ammonia, but a portion of the aricine remains dissolved in excess of ammonia, from which it crystallises: the precipitate, which is amorphous at first, likewise becomes crystalline after a few days. The salts are precipitated by iodide of potassium, bichloride of platinum, chloride of gold, and tannic acid (Manzini).

*Sulphate of Aricine.* — A. *Neutral?* — A neutral solution of aricine in dilute sulphuric acid solidifies on cooling to a white tremulous jelly, which dries up to a horny mass on exposure to the air, and is again converted into a jelly by boiling water. A solution of the salt in alcohol yields silky needles, dull according to Winckler, resembling those of sulphate of quinine. The crystals dissolve in warm water [less easily than sulphate of cinchonine, more easily than sulphate of quinine (Winckler)], and again gelatinise on cooling. The salt is insoluble in ether (Pelletier & Coriol).

B. *Acid.* — Flat needles (Pelletier); crystals, obtained by dissolving aricine in a slight excess of sulphuric acid. Does not lose weight at 210° (Manzini). The solution exhibits a blue fluorescence (Winckler).

|  |  |  |  |  | Manzini. |
|---|---|---|---|---|---|
| 46 C | 276 | ........ | 56·09 | ........ | 55·59 |
| 2 N | 28 |  | 5·69 |  |  |
| 28 H | 28 | ........ | 5·69 | ........ | 6·07 |
| 10 O | 80 | ........ | 16·27 |  |  |
| 2 SO³ | 80 | ........ | 16·26 | ........ | 16·68 |
| C$^{46}$N$^2$H$^{26}$O$^8$,2(HO,SO³) | 492 | ........ | 100·00 |  |  |

*Hydriodate of Aricine.* — A solution of aricine in warm dilute acid yields, on cooling, lemon-yellow needles, very slightly soluble in cold, easily soluble in warm alcohol. The crystals do not change at 200°, but cake together at 220°, and melt to a dark mass at 250° (Manzini).

|  | at 120° |  |  |  | Manzini. |
|---|---|---|---|---|---|
| C$^{46}$N$^2$H$^{26}$O$^8$ | 394 | ........ | 75·48 |  |  |
| HI | 128 | ........ | 24·52 | ........ | 24·54 |
| C$^{46}$N$^2$H$^{26}$O$^8$,HI | 522 | ........ | 100·00 |  |  |

*Hydrochlorate of Aricine.* — When aricine is exposed to a current of hydrochloric acid gas at 120°, 100 parts of it take up 8·52 parts of hydrochloric acid (1 at. = 9·26 parts HCl). The mass becomes warm, without melting, assumes a yellow, afterwards dark-orange colour, and when dissolved in alcohol and evaporated, leaves an amorphous brown gum. — A solution of aricine in warm aqueous hydrochloric acid

yields, on cooling, crystals which lose their water of crystallisation in a vacuum, and nothing more at 120° (Manzini).

|  | | *at* 130°. | | | Manzini. |
|---|---|---|---|---|---|
| $C^{46}N^2H^{26}O^8$ | ............ | 394 | ........ | 91·76 | |
| HCl | ............... | 36·5 | ........ | 8·24 | ........ 8·33 |
| $C^{46}N^2H^{26}O^8,HCl$ | .... | 430·5 | ........ | 100·00 | |

*Chloroplatinate of Aricine.* — Lemon-yellow precipitate, very slightly soluble in water, but easily soluble in alcohol, from which it crystallises on spontaneous evaporation (Manzini).

|  | *at* 120°. | | | Manzini. |
|---|---|---|---|---|
| $C^{46}N^2H^{26}O^8$ | ..................... 394 | ........ | 65·67 | |
| $HCl^3$ | ..................... 107·5 | ........ | 17·91 | |
| Pt | ..................... 98·7 | ........ | 16·42 | ........ 16·31 |
| $C^{46}N^2H^{26}O^8,HCl,PtCl^2$ | ........ 600·2 | ........ | 100·00 | |

Aricine dissolves in *alcohol* more easily than cinchonine, less easily than quinine (Winckler). It is soluble in *ether*.

### Appendix to Aricine.

## Paricine.

F. L. WINCKLER. *Repert.* 91, 145; 92, 29, and 231; *N. Repert.* 1, 11.

To be distinguished from aricine. Discovered by Winckler in 1845 in *China Jaen fusca* from Para (Wiggers, 404), and at first mistaken for aricine (p. 568), but afterwards found to be an independent body. — It occurs also in a bark resembling *Cortex caribæus* [*China de Para rubra?* (Kr.)] (Winckler, *Repert.* 96, 341).

*Preparation.* The finely powdered bark is exhausted by thrice boiling it with three times its weight of 80 p. c. alcohol. The extracts thus obtained are freed from the greater part of the alcohol by distillation, and the residue is evaporated to dryness, triturated, and digested with warm hydrochloric acid containing $\frac{1}{30}$th of the fuming acid, which leaves a portion undissolved. The dissolved paricine is precipitated with carbonate of soda, washed, dried, dissolved in ether, and recovered from the solution by evaporation; then dissolved in very dilute hydrochloric acid, treated with animal charcoal, and again precipitated with carbonate of soda. The portion remaining undissolved in the first treatment with dilute hydrochloric acid may be freed from a red compound by heating it with aqueous carbonate of soda, after which acids take up more paricine from the residue. Paricine thus obtained leaves a slight residue when dissolved in dilute sulphuric acid.

*Properties.* Yellow amorphous resinous mass. *Hydrate of paricine,* containing 5·03 p. c. of water, precipitated from the acid solutions by ammonia or alkalis, forms a white, very loose powder. Tastes very bitter.

According to the (preliminary) analyses of Weidenbusch, paricine is represented by the formula $C^{46}N^2H^{25}O^6$: the phosphate, hydrochlorate and chromate contain, in combination with the amount of paricine represented by this formula, 1 atom of acid and 1 atom of water.

Paricine is coloured greenish-yellow, afterwards a fine dark-green by *nitric acid* of sp. gr. 1·4; also by oil of vitriol, and is decomposed by the latter acid.

It is wetted with difficulty by water, and dissolves very slightly. — It is soluble in dilute *acids* (more slowly after drying), forming colourless or yellow amorphous salts. The sulphate and hydrochlorate are precipitated from their neutral solutions by hydrochloric, nitric, or sulphuric acid, the precipitates being soluble in water.

*Phosphate of Paricine.* — Precipitated from the hydrochlorate by phosphate of soda. Resembles the hydrate (Winckler). Contains 14·86 p. c. PO⁵, and 2·06 p. c. of water (Weidenbusch).

*Sulphate of Paricine.* — A solution of paricine in warm dilute sulphuric acid solidifies on cooling to a firm jelly, which dries up to a brown, translucent, horny mass, turning opaque when warmed, triturable to a white powder, and containing, after drying at 100°, 7·79 p. c. of sulphuric acid (Winckler).

*Hydrochlorate of Paricine.* — A solution of paricine in hydrochloric acid leaves on evaporation a colourless friable resin, which, according to Weidenbusch, contains 8·53 p. c. of water.

*Chromate of Paricine.* — Contains 2·3 p. c. of water, and 16·4 p. c. of chromic acid (Weidenbusch).

Hydrochlorate of paricine precipitates *mercuric chloride* (Winckler). It throws down a yellowish-white amorphous precipitate from *iodomercurate of potassium* (Delffs).

*Chloroplatinate of Paricine.* — Resembles the quinine·salt. Burns vigorously when heated. Contains 3 p. c. of water, and 15 to 16 p. c. of platinum (Winckler).

Paricine dissolves easily in *alcohol* and *ether*.


# Brucine.

$$C^{46}N^2H^{26}O^8 = C^{46}N^2H^{24}O^8,H^2.$$
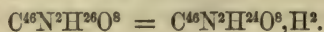
PELLETIER & CAVENTOU. *Ann. Chim. Phys.* 12, 113; *J. Pharm.* 2, 529; *Schw.* 28, 32; *Gilb.* 63, 322; *Ann. Chim. Phys.* 26, 53.
MERCK. *N. Tr.* 20, 1, 134.
DUFLOS. *Schw.* 62, 68.
LIEBIG. *Pogg.* 21, 22, and 487. — *Ann. Pharm.* 26, 53; 29, 62.
REGNAULT. *Ann. Pharm.* 26, 20; *J. pr. Chem.* 16, 267. — *Ann. Pharm.* 29, 59.
PELLETIER. *Ann. Chim. Phys.* 63, 176; *Ann. Pharm.* 22, 121. — *J. Pharm.* 24, 159; *Ann. Pharm.* 29, 53; *J. pr. Chem.* 14, 180. — *Ann. Chim. Phys.* 54, 186.
VARRENTRAPP & WILL. *Ann. Pharm.* 39, 285.

DOLLFUSS. *Ann. Pharm.* 65, 214; *Kopp's Jahresber.* 1847 and 1848, 629.

STRECKER. *Ann. Pharm.* 91, 76; *N. Ann. Chim. Phys.* 42, 366; *Kopp's Jahresber.* 1854, 520.

Discovered by Pelletier & Caventou in 1819. — Occurs in the bark of *Strychnos Nux vomica* and in false angustura bark; also, together with strychnine, in *Nux vomica*, sparingly in Ignatius' beans and in Upas Tieuté. See p. 480. — A South American arrow poison from Cuenia, known as *Cuba longa*, contains brucine, but no strychnine (Palm, *Pharm. Viertelj.* 11, 552).

*Preparation.* 1. *From Nux vomica.* — In the preparation of strychnine by the method described at p. 480, brucine remains dissolved, together with colouring matter, in the alcohol of 34 p. c. employed, and is obtained as sulphate by evaporating the alcoholic solution to a syrup, neutralising with cold dilute sulphuric acid, and setting the liquid aside for some days; the salt then crystallises, and is to be separated from the black mother-liquor by pressing. The crystals are dissolved in water, and the solution is decolorised with animal charcoal and precipitated by ammonia, which throws down a portion of the brucine, the remainder crystallising from the ammoniacal liquid on exposure to the air. The crystals are purified by recrystallisation from boiling alcohol of 80 p. c. (Coriol & Soubeiran, *N. J. Pharm.* 45, 231). — Wittstein (*Darstell. und Prüfung*, 215) evaporates the alcoholic mother-liquor of strychnine to dryness with a quantity of binoxalate of potash amounting to $\frac{1}{50}$th of the weight of the nux vomica employed, then triturates the residue, and digests it for two days with absolute alcohol at 0°. The undissolved portion is again washed with ice-cold absolute alcohol so long as it imparts a colour thereto, and is then dissolved in warm water, heated to volatilise the whole of the alcohol, and agitated for several days with a quantity of magnesia equal to $\frac{1}{100}$th of the weight of the nux vomica employed. The precipitate thereby produced is collected and exhausted with 90 p. c. alcohol, and the tincture is concentrated and placed in the cold; the brucine then collects at the bottom in the form of an oil, which afterwards crystallises. In this way 10 pounds of nux vomica yield 6 drachms of brucine (Wittstein).

2. *From false Angustura bark.* — The bark is freed from fat by ether, and boiled repeatedly with alcohol; the tincture is evaporated and the residue dissolved in water; the greater part of the colouring matter is precipitated with basic acetate of lead; the liquid is filtered and freed from excess of lead by hydrosulphuric acid; and the filtrate is boiled to throw down a little strychnine, mixed with a quantity of magnesia equal to $\frac{1}{50}$th of the bark, again filtered, and evaporated: a granular mass of brucine then remains, together with colouring matter. The brucine thus obtained is converted into oxalate by the addition of oxalic acid, and the salt is treated with ice-cold absolute alcohol, which takes up colouring matter. The remaining pure oxalate of brucine is decomposed by evaporating it with magnesia and water, and the dry mass is exhausted with alcohol and the tincture evaporated to crystallisation (Pelletier & Caventou).

The hydrated crystals are still to be freed from water by heating.

*Properties.* Anhydrous brucine melts a little above 100° to a colourless liquid, which solidifies to a brittle wax on cooling. See further *Hydrated Brucine.*

Very small quantities of brucine cautiously heated on platinum foil in the manner described under strychnine (p. 484), yield on the superposed glass plate, a whitish deposit, in which round granules are visible under a magnifying power of 80 diameters; but if the brucine is too strongly heated, fatty drops also make their appearance. On addition of water, the granules collect in denser groups without becoming crystalline: aqueous ammonia likewise produces no crystals but unites the granules in deep-yellow oily drops. Strong nitric acid colours the granules deep orange-yellow; dilute nitric, hydrochloric, or sulphuric acid produces crystalline formations which rapidly disappear. Dilute chromic acid dissolves the granules only slowly and incompletely, but produces dark-yellow prisms and stars at the edges of the microscopic drops (Helwig, *Anal. Zeitschr.* 3, 49).

| | | | Dumas & Pelletier. | Liebig. | Regnault. | Ettling. | Strecker. |
|---|---|---|---|---|---|---|---|
| 46 C | 276 | 70·00 | 74·11 | 69·90 | 69·95 | 69·88 | 70·00 |
| 2 N | 28 | 7·10 | 7·22 | 5·07 | 7·07 | | |
| 26 H | 26 | 6·64 | 6·52 | 6·66 | 6·77 | 6·75 | 6·70 |
| 8 O | 64 | 16·26 | 12·15 | 18·37 | 16·21 | | |
| $C^{46}N^2H^{26}O^8$ | 394 | 100·00 | 100·00 | 100·00 | 100·00 | | |

The above formula was established by Regnault and Dollfus. Earlier formulæ: $C^{24}NH^{12}O^3$ (Dumas & Pelletier); $C^{32}NH^{18}O^6$, afterwards $C^{47}N^2H^{27}O^8$ (Liebig); $C^{48}N^2H^{24}O^8$ (Regnault); $C^{44}N^2H^{25}O^7$ (Varrentrapp & Will). — Isomeric with aricine (p. 568).

*Decompositions.* 1. Brucine *heated* above its melting point yields combustible gas and a very little carbonic acid, together with water, acetic acid, and a large quantity of empyreumatic oil, but no ammonia (Pelletier and Caventou). — 2. When melted on platinum-foil and then more strongly heated, it *takes fire*, and leaves a bulky, easily combustible cinder (Merck). — 3. In the decomposition of its salts by *electrolysis*, there appears at the positive pole the red colour which is likewise produced by the action of nitric acid (Pelletier & Couerbe). It behaves in the same way as morphine (xvi, 425) (Hlasiwetz & Rochleder). — 4. It forms a peculiar compound with *iodine* (see below). — *Bromine* forms with it bromobrucine (Laurent). Bromine-water produces a brown precipitate in aqueous brucine (Duflos). — 5. *Chlorine gas* passed into water in which brucine is suspended dissolves the brucine, forming a yellow neutral liquid which turns acid and assumes a rose-red to blood-red colour, and afterwards loses its colour and deposits a small quantity of yellowish flocks. When neutralised with ammonia and evaporated, it leaves sal-ammoniac, coloured red; from the blood-red solution ammonia throws down an amorphous, bitter, non-poisonous resin. Aqueous hydrochlorate of brucine is likewise coloured by chlorine, without forming an insoluble product, as is the case with strychnine (Pelletier), so that traces of strychnine may be detected in brucine by the cloudiness produced on passing chlorine into the solution for ten minutes (Lepage, *J. Pharm.* 26, 140). Chlorine-water colours solutions of brucine-salts a fine pale-red, which is changed to yellowish-brown by ammonia.

6. Brucine is not coloured by cold *oil of vitriol*, but assumes a yellow

colour with the hot liquid (Kersting; Guy, *Anal. Zeitschr.* 1, 92). See below. — 7. On boiling a strong solution of the hydrochlorate with *nitrite of potash*, it evolves a large quantity of gas burning with a green-edged flame (A. W. Hofmann, *Ann. Pharm.* 75, 368).

8. Brucine assumes a dark-red colour when *nitric acid* of sp. gr. 1·4 is poured upon it (Pelletier & Caventou), becoming hot and dissolving, with evolution of combustible gas, the residue solidifies, on cooling, to an orange-coloured mass, from separation of cacotheline (Gerhardt). When the cacotheline is allowed to remain in contact with the nitric acid mother-liquor for a few hours, it is converted into another chrome-yellow body, which is insoluble in water and explodes when heated (Gerhardt). — The gas evolved is a mixture of nitrite of methyl (1 atom of which is produced from 1 atom of brucine), nitric oxide, and carbonic acid, the last being formed from oxalic acid, which occurs, together with cacotheline, in the residue. In this reaction 1 atom of brucine yields 4 atoms of carbon in the form of oxalic or carbonic acid :
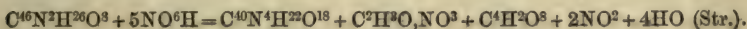
$$C^{46}N^2H^{26}O^8 + 5NO^6H = C^{40}N^4H^{22}O^{18} + C^2H^3O,NO^3 + C^4H^2O^8 + 2NO^2 + 4HO \text{ (Str.)}.$$
Brucine.        Cacotheline.     Methylic     Oxalic
                                     nitrite.      acid.

Gerhardt regarded the combustible gas as nitrite of ethyl, free from nitric oxide and carbonic acid; and according to Laurent, the gas does not contain carbonic acid. Liebig, by warming the mixture of acid and brucine, obtained, instead of nitrite of methyl, a liquid condensable in a freezing-mixture, boiling at 70° to 75°, not miscible with water, and heavier than dilute nitric acid : according to Strecker this body is probably nitrate of methyl obtained by the employment of more dilute nitric acid. Laurent condensed the gas obtained from brucine and nitric acid to a liquid which distilled at 10° to 16°, burned with flame, evolving nitrous fumes, and contained carbon and hydrogen in the same proportion as nitrite of ethyl. This body was perhaps a mixture of nitrite and nitrate of methyl (Kr.). See Liebig (*Ann. Pharm.* 57, 94, and 58, 234) and Gerhardt, Laurent, and Rosengarten, in the memoirs referred to under cacotheline (p. 358).

The fine red solution of brucine in excess of nitric acid is decolorised by hydrosulphuric acid, sulphurous acid, or protochloride of tin; it turns yellow on warming or on further addition of nitric acid, whereupon protochloride of tin [and hydrosulphate of ammonia (Fresenius)] immediately produces a splendid violet coloration and precipitate (Pelletier & Caventou). Fuming nitric acid dissolves brucine, with considerable intumescence, forming a red solution : nitric acid of sp. gr. 1·2 dissolves it with gradually deepening brown-red colour (Duflos).

When a layer of a solution of brucine in 1,000 parts of water is placed upon an equal bulk of oil of vitriol, there is formed, in presence of traces of *nitric acid*, a rose-red zone which quickly changes to yellow at the lower edge. This reaction may be employed for the detection of very small quantities of nitric acid (Kersting, *Ann. Pharm.* 125, 254). — Brucine covered with oil of vitriol containing nitric acid, prepared as described at p. 141, vol. xvi, is coloured a transient red, changing to yellow; the addition of a few drops of water hastens the formation of the yellow colour. The solution is again turned red, afterwards yellow by the addition of particles of oxide of manganese, and assumes a golden yellow colour when nearly

neutralized or when supersaturated with ammonia (J. Erdmann, *Ann. Pharm.* 120, 188). Brucine prepared from *nux vomica* is coloured rose-red, orange, and olive-green by oil of vitrol (containing nitric acid ?) : brucine from false angustura bark exhibits purer colours which change, not to green but to deep-yellow (Merck). Other oxidising bodies (see xvi, 141), added to the sulphuric acid solution, produce a red coloration in the same way as nitric acid (Lefort, *Rev. scient.* 16, 355). Permanganate of potash colours the solution in sulphuric acid red, brown, orange, and yellow (Guy); chromate of potash colours it dark-green, with evolution of gas ; peroxide of lead produces no effect (Riegel, *N. Br. Arch.* 58, 279).

9. When 1 part of crystallised brucine is carefully heated with 10 parts of water, 4½ parts of *oil of vitriol,* and *oxide of manganese,* an evolution of inflammable vapours, probably of methyl-alcohol, takes place, attended with frothing of the mass. Peroxide of lead, mercuric oxide, and chromate of potash, employed instead of oxide of manganese, act in the same way, but on warming 1 part of brucine with bichromate of potash, 2 parts of oil of vitriol, and 2½ parts of water, carbonic and formic acids are also produced (Baumert, *Ann. Pharm.* 70, 337).

The volatile product possesses the following properties. It has a suffocating odour, and like the product formed by the action of nitric acid on brucine, is colourless, oily, easily inflammable, and burns with a blue, slightly luminous flame (Liebig, *Ann. Pharm.* 65, 114). It reduces nitrate of silver, but is not affected by potash-ley, and is, therefore, free from aldehyde (Rosengarten, *Ann. Pharm.* 65, 114). When freed from formic acid by rectification over chalk, and dehydrated as far as possible, without warming, by carbonate of potash, and afterwards by chloride of calcium, it forms a transparent, colourless liquid, which has an aromatic odour, burns with blue flame, and throws down metallic silver when boiled with nitrate of silver and baryta-water, yielding a volatile acid in combination with baryta. It has the following composition :—

|  |  |  | | Baumert. | | | Merck. | |
|  |  |  | *a.* | | *b.* | | *a.* | *b.* |
|---|---|---|---|---|---|---|---|---|
| 2 C | 12 | 37·5 | | 33·85 | | 31·15 | 34·5 | 37·8 |
| 4 H | 4 | 12·5 | | 12·36 | | 12·41 | 12·2 | 12·4 |
| 2 O | 16 | 50·0 | | 53·79 | | 56·44 | 53·3 | 49·8 |
| C²H⁴O² | 32 | 100·0 | | 100·00 | | 100·00 | 100·0 | 100·0 |

*a* was rectified once, *b* twice, over chloride of calcium. The body is, therefore, methylic alcohol, not quite free from water.

10. Brucine, acted upon by *peroxide of lead* and *dilute sulphuric acid,* yields a brown amorphous body, soluble in alcohol, and a black, or in thin layers, red, amorphous body, insoluble in alcohol, both of which are coloured red or yellowish-red by strong nitric acid and by oil of vitriol (E. Marchand, *N. J. Pharm.* 4, 28 ; *J. Chim. méd.* 20, 367).

11. Brucine forms derivatives with *iodide of methyl* (Stahlschmidt), *iodide of ethyl* (Gunning), and *bibromide of ethylene* (Schad). — 12. It is not decomposed by the alcoholic fermentation of sugar, or by putrefaction (Larocque & Thibierge, *J. Chim. méd.* 18, 689).

*Combinations.* — A. *With Water.* 1. *Hydrated Brucine.* — Crystallises on slowly evaporating an alcoholic solution mixed with water in

transparent oblique four-sided prisms (Pelletier & Caventou), or in radiated groups of needles (Merck). By rapid evaporation pearly laminæ, resembling boracic acid, are obtained (Pelletier & Caventou). — Has a powerful and persistent bitter taste. Poisonous, though less so than strychnine. — Rotates a ray of polarised light to the left ; $[\alpha]r$ in transparent crystals = 61·27°, in slightly effloresced crystals = 64·48°, both in alcoholic solution ; in solution in hydrochloric acid the rotation is only = 13·97°, but it is restored to the original amount by ammonia (Bouchardat, N. Ann. Chim. Phys. 9, 213).

Brucine gives off the whole of its water of crystallisation in a vacuum over oil of vitriol (Strecker), or when heated to 130°, or till it melts, forming anhydrous brucine.

| | Crystals. | | | Regnault. | | Liebig. | | Varrentrapp & Will. |
|---|---|---|---|---|---|---|---|---|
| $C^{46}N^2H^{26}O^8$ | 394 | .... | 84·55 | | | | | |
| 8 HO | 72 | .... | 15·45 | .... | 15·45 | .... | 16·66 | .... | 14·60 |
| $C^{46}N^2H^{26}O^8 + 8aq.$ | .... | 466 | .... | 100·00 | | | | |

Or

| | | Crystals. | | | | Regnault. | Varrentrapp & Will. |
|---|---|---|---|---|---|---|---|
| 46 C | | 276 | ........ | 59·22 | ........ | 59·00 | |
| 2 N | | 28 | ........ | 6·01 | ........ | | 6·65 |
| 34 H | | 34 | ........ | 7·29 | ........ | 7·29 | |
| 16 O | | 128 | ........ | 27·48 | | | |
| $C^{46}N^2H^{26}O^8 + 8aq.$ | .... | 466 | ........ | 100·00 | | | |

According to Pelletier & Dumas, brucine crystallised from water contains 18·5 p. c., whilst that crystallised from alcohol contains 13·5 p. c., of water of crystallisation.

2. *Aqueous solution.* — Brucine dissolves in 850 parts of cold, and in 500 parts of boiling *water* (Pelletier & Caventou) ; in 768 parts of water at 18·75° (Abl). Crystallised brucine dissolves in 320 parts of cold, and in 150 parts of boiling water (Duflos).

Brucine is insoluble in *ammonia-water* (Merck): potash and ammonia render it less soluble in water. It is precipitated from its aqueous solution by potash-ley immediately, and by carbonate of potash on standing for a short time (Duflos).

B. *With Iodine.* — Tincture of iodine throws down from brucine-salts a dense kermes-brown or chocolate-brown precipitate, which dissolves to a pale-brown liquid when heated (Simon, *Repert.* 65, 194 ; v. Planta). The orange-brown precipitate produced by biniodide of potassium in solutions of acetate of brucine, even when dilute, dissolves in caustic potash, but not in acetic acid (Wormley).

A. *With* $1\frac{1}{2}$ *atoms of Iodine.* — Brown precipitate, thrown down from cold alcoholic brucine by tincture of iodine, not in excess (Pelletier). According to Regnault it crystallises in laminæ.

| | | | | Pelletier. | | |
|---|---|---|---|---|---|---|
| 2 $C^{46}N^2H^{26}O^8$ | ........ | 788 | ........ | 67·41 | | |
| 3 I | ................ | 381 | ........ | 32·59 | ........ | 33·41 |
| 2 $C^{46}N^2H^{26}O^8,3I$ | .... | 1169 | ........ | 100·00 | | |

B. *With 3 atoms of Iodine.* — Brucine turns brown when triturated

with iodine and water, and forms, on boiling, a soft resin, which gives up only traces to water, dissolves completely in boiling alcohol, forming a solution which deposits iodobrucine as a brown powder on cooling, and afterwards yields white crystals of hydriodate of brucine. — Iodobrucine turns red with strong nitric acid and with nitrate of silver (Pelletier). According to Regnault, this compound likewise crystallises in laminæ.

|  |  |  |  |  |  | Pelletier. | Regnault. |
|---|---|---|---|---|---|---|---|
| 46 C | ............... | 276 | ........ | 35·62 | ........ | ........ | 36·14 |
| 2 N | ............... | 28 | ........ | 3·62 | | | |
| 26 H | ............... | 26 | ........ | 3·35 | ........ | ........ | 3·55 |
| 8 O | ............... | 64 | ........ | 8·25 | | | |
| 3 I | ............... | 381 | ........ | 49·16 | ........ | 45·60 | |
| $C^{46}N^2H^{26}O^8,3I$ | .... | 775 | ........ | 100·00 | | | |

C. *With Acids.* — Brucine neutralises acids completely, forming very bitter, generally crystallisable salts. From aqueous solutions of brucine-salts, the alkalis, magnesia, morphine, and strychnine throw down the brucine by combining with the acid. The precipitate produced by caustic potash and its carbonate is dense, pulverulent, and insoluble in excess of the precipitant: it is converted, by combining with water, into concentrically arranged needles, visible to the naked eye. Ammonia throws down oily drops, which dissolve in an excess of ammonia added at the same time, and crystallise from the solution in needles: the oily drops are likewise rapidly converted into needles (Fresenius). When the addition of ammonia produces an evolution of heat, the brucine is thrown down as an oil, which in a day or two takes up water and becomes crystalline (Pelletier & Caventou). Bicarbonate of soda produces in solutions of brucine-salts, after standing for some time, a deposit of needles, which are insoluble in excess of the precipitant, but dissolve in the carbonic acid set free on adding to the liquid a quantity of hydrochloric acid insufficient to decompose the whole of the carbonate. Bicarbonate of soda throws down larger crystals from acid solutions, but only when the carbonic acid begins to escape (Fresenius). A solution of brucine in 200 to 500 parts of water containing tartaric acid is not precipitated by alkaline bicarbonates after addition of tartaric acid (Oppermann).

*Carbonate of Brucine.* — The very easily formed solution of brucine in water containing carbonic acid deposits crystals free from carbonic acid, having a pearly lustre and arranged in long feathery forms. Alkaline carbonates added to brucine-salts likewise precipitate brucine free from carbonic acid (Langlois, *Ann. Chim. Phys.* 48, 502; *Ann. Pharm.* 100, 374).

*Phosphate of Brucine.* — Aqueous phosphoric acid neutralised with brucine does not yield crystals when evaporated: in presence of an excess of acid, the solution very easily yields large rectangular tables, the ends of which are formed by truncation-faces; the crystals are slightly efflorescent in dry air and easily soluble in water (Pelletier & Caventou). — Phosphate of soda produces no precipitate in nitrate of brucine; it produces slight flocks in the sulphate, and throws down long thin needles from the hydrochlorate after 12 hours or more (v. Planta).

By concentrating and cooling a solution of brucine in aqueous phosphoric acid, Anderson (*Ann. Pharm.* 66, 58) obtained short thick

prisms which effloresce in the air, melt in their water of crystallisation at 100°, and solidify to a resinous mass on cooling. They dissolve in all proportions in hot and somewhat freely in cold water.

| | | | | | | Anderson. |
|---|---|---|---|---|---|---|
| 92 C | 552 | ........ | 61·61 | ........ | 62·05 |
| 4 N | 56 | ........ | 6·25 | | |
| 55 H | 55 | ........ | 6·14 | ........ | 6·51 |
| 19 O | 152 | ........ | 18·08 | | |
| PO⁵ | 71 | ........ | 7·92 | | |

$2 \, C^{46}N^2H^{26}O^8,3HO,PO^5$ ........ 896 ........ 100·00

By digesting aqueous *monosodic phosphate with brucine*, short thick prisms of a double salt having the formula $C^{46}N^2H^{26}O^8,NaO,2HO,PO^5$ are obtained (Anderson).

*Hyposulphite of Brucine.* — Formed in a mixture of brucine, hydrosulphate of ammonia, and alcohol on standing in the air. — Prismatic needles which lose 1·79 p.c. of water in a vacuum over oil of vitriol (1 at. = 1·8 p. c. HO). Dissolves in 105 parts of cold water (How, *Pharm. Centr.* 1855, 95).

| | In a vacuum. | | | How. | |
|---|---|---|---|---|---|
| 46 C | 276 | ........ | 56·67 | ........ | 56·68 |
| 2 N | 28 | ........ | 5·74 | | |
| 31 H | 31 | ........ | 6·36 | ........ | 6·58 |
| 15 O | 120 | ........ | 24·66 | | |
| 2 S | 32 | ........ | 6·57 | — | |

$C^{46}N^2H^{26}O^8,HO,S^2O^2 + 4aq$ .... 487 ........ 100 00

*Sulphate of Brucine.* — A. *Neutral.* Long, apparently four-sided very bitter needles, easily soluble in water and slightly soluble in alcohol (Pelletier & Caventou). Loses at 130°, 12 p.c. (Regnault), 12·33 p. c. of water (Varrentrapp & Will) (7 at. = 12·25 p.c. HO).

| | Dried. | | | Regnault. | Varrentrapp & Will. |
|---|---|---|---|---|---|
| 46 C | 276 | ........ | 62·30 | ........ | 61·86 | |
| 2 N | 28 | ........ | 6·32 | ........ | 6·38 | |
| 27 H | 27 | ........ | 6·09 | ........ | 6·53 | |
| 9 O | 72 | ........ | 16·25 | ........ | 16·45 | |
| SO³ | 40 | ........ | 9·04 | ........ | 8·78 | ........ 8·87 |

$C^{46}N^2H^{26}O^8,HO,SO^3$ .... 443 ........ 100·00 ........ 100·00

The air-dried salt contains 54·14 p.c. C., and 6·62 H. (Liebig) (calc. 54·54 p. c. C., 6·71 H.).

B. *Acid.* — On adding sulphuric acid to a concentrated solution of the neutral salt, large crystals are rapidly formed from which ether takes up the excess of acid not required for the formation of the acid salt (Pelletier & Caventou).

*Periodate of Brucine.* — Obtained from periodic acid and alcoholic brucine. Fine colourless needles producing a faint explosion when heated (Langlois, *N. Ann. Chim. Phys.* 34, 278). Dissolves easily in water and alcohol, forming solutions which undergo alteration in the air (Bödeker, *Ann. Pharm.* 71, 64).

*Iodate of Brucine.* — Iodic acid and iodate of potash produce neither coloration nor precipitate in aqueous brucine-salts (Simon; v. Planta). The colourless salt obtained by neutralising aqueous iodic acid with brucine breaks up on evaporation into opaque silky crystals of a basic salt and hard four-sided prisms of an acid salt (Pelletier). By dissolving brucine in iodic acid Serullas (*Ann. Chim. Phys.* 45, 274) obtained a red liquid which did not yield distinct crystals, according to Pelletier, because he employed an excess of acid.

*Hydriodate of Brucine.* — Iodide of potassium throws down from solutions of acetate of brucine [containing $\frac{1}{500}$th or more of the salt (Wormley)] a crystalline precipitate which after washing with water crystallises from alcohol in silky needles, soluble in a large quantity of ammonia-water (Merck). Iodide of potassium throws down from the hydrochlorate or nitrate, needles or laminæ, and from the sulphate, hard prisms (v. Planta). — Transparent, four-cornered laminæ, or very short prisms obtained from iodide of potassium and sulphate of brucine, or by neutralising hydriodic acid with brucine. Dissolves more freely in alcohol than in water (Pelletier).

|  | | Crystals. | | | Pelletier. |
|---|---|---|---|---|---|
| 46 C | ........................ | 276 | ........ | 52·87 | ........ 53·62 |
| 2 N | ........................ | 28 | ........ | 5·36 | |
| 27 H | ........................ | 27 | ........ | 5·17 | |
| 8 O | ........................ | 64 | ........ | 12·26 | |
| I | ...  ................... | 127 | ........ | 24·34 | ........ 23·57 |
| C⁴⁶N²H²⁶O⁸,HI | .... | 522 | ........ | 100·00 | |

*Perchlorate of Brucine.* — Pale-yellow shining prisms, obtained by neutralising dilute aqueous perchloric acid with brucine. The crystals give off 5·4 p. c. water at 170°, and detonate when more strongly heated. — Dissolves very slightly in cold water and alcohol, and less freely than the corresponding strychnine-salt in the hot liquids (Bödeker, *Ann. Pharm.* 71, 62 ; *Kopp's Jahresber.* 1849, 382).

*Chlorate of Brucine.* — Chlorate of potash does not precipitate nitrate of brucine (Simon). By dissolving brucine in warm aqueous chloric acid, a red liquid is obtained, which deposits transparent rhombohedrons resembling calc-spar. The crystals may be obtained free from colour by recrystallisation. Explodes when heated. Dissolves less easily in water than chlorate of strychnine (Serullas, *Ann. Chim. Phys.* 45, 280).

*Hydrochlorate of Brucine.* — 100 parts of dry brucine take up 13·06 parts of hydrochloric acid gas, and form a mass soluble without residue in water (Liebig); at a temperature of 130°, however, only 9·29 parts of hydrochloric acid are retained (Regnault) (calc. 9·26 parts HCl).— By dissolving brucine in warm aqueous hydrochloric acid, four-sided obliquely truncated prisms and needles [small tufts of needles (Regnault)] are obtained on cooling (Pelletier & Caventou). The salt is permanent in the air, and dissolves very easily in water (Pelletier & Caventou). It dissolves freely in warm creosote (Reichenbach).

|  | | Dried. | | | Regnault. |
|---|---|---|---|---|---|
| 46 C | ........................ | 276 | ........ | 64·11 | ........ 63·88 |
| 2 N | ........................ | 28 | ........ | 6·50 | ........ 6·54 |
| 27 H | ........................ | 27 | ........ | 6·27 | ........ 6·81 |
| 8 O | ........................ | 64 | ........ | 14·86 | ........ 14·96 |
| Cl | ........................ | 35·5 | ........ | 8·26 | ........ 7·81 |
| C⁴⁶N²H²⁶O⁸,HCl | .... | 430·5 | ........ | 100·00 | ........ 100·00 |

*Hydrofluate of Brucine.* — A solution of brucine in warm, moderately strong hydrofluoric acid yields on cooling, small, colourless, right rhombic prisms, which give off 3·34 p. c. of water at 100°. — The salt dissolves in water, but is nearly insoluble in cold, and but slightly soluble in boiling alcohol (Elderhorst, *Ann. Pharm.* 74, 79 ; *Kopp's Jahresber.* 1850, 432).

*Nitrate of Brucine.* — A neutral solution of brucine in nitric acid yields on evaporation an amorphous gum ; an acid solution readily yields large, hard four-sided prisms, with dihedral summits. When heated the salt turns red and black, and then takes fire with slight explosion (Pelletier & Caventou). — Loses 7·23 p. c. of water at 130° (Regnault) (4 at. = 7·32 p. c. HO).

|  |  | Dried. |  |  |  | Regnault. mean. |
|---|---|---|---|---|---|---|
| 46 C | | 276 | ........ | 60·39 | ........ | 60·50 |
| 3 N | | 42 | ........ | 9·19 | ........ | 8·92 |
| 27 H | | 27 | ........ | 5·90 | ........ | 6·06 |
| 14 O | | 112 | ........ | 24·52 | ........ | 24·52 |
| $C^{46}N^2H^{26}O^8,HO,NO^5$ .... | | 457 | ........ | 100·00 | ........ | 100·00 |

*Phosphantimonic acid* (xiv, 227) throws down from aqueous hydrochlorate of brucine, even in dilute solutions, a fine rose-red precipitate, which dissolves when heated, and reappears on cooling, the liquid then acquiring a deep crimson colour (F. Schulze, *Ann. Pharm.* 109, 179). — *Phosphomolybdic acid* (xiii, 164) throws down ochre-yellow flocks (Sonnenschein); an orange-yellow precipitate, insoluble in nitric acid, but soluble in aqueous ammonia with yellowish-green colour, turning brown on boiling, and also in alkalis (Trapp, *Russ. Pharm. Zeitschr.* 2, 1 ; *Kopp's Jahresber.* 1863, 702).

*Chromate of Brucine.* — The neutral and acid chromate of potash throw down from acetate of brucine (even from solutions containing only $\frac{1}{1000}$th of the alkaloïd) yellow needles, insoluble in acetic acid (Wormley). Neutral chromate of potash and sulphate of brucine yield small, pale-yellow prisms, of a neutral salt, which reddens in sunshine. Chromic acid and brucine form micaceous crystals of an acid salt, easily decomposed by light (André, *N. J. Pharm.* 41, 341; *Zeitschr. Ch. Pharm.* 5, 651). — Much more easily soluble in water than the corresponding strychnine-salts (Horsley).

Brucine partly decomposes the sulphates of *iron* and *copper*, forming double salts (Pelletier & Caventou). — Sulphate of brucine does not combine with ferric sulphate to form a double salt (Will, *Ann. Pharm.* 42, 111).

*Iodomercurate of potassium* throws down from brucine-salts, a white or yellow powder, which quickly cakes together in curdy masses, not perceptibly soluble in hydrochloric acid (v. Planta ; Delffs). Brucine, iodide of potassium, and mercuric chloride yield a double compound, corresponding to that obtained with strychnine (p. 497), somewhat soluble in water (Groves).

*Chloromercurate of Brucine.* — Mercuric chloride throws down from hydrochlorate of brucine (from the sulphate or nitrate only after addition of chloride of sodium) a dense, opaque precipitate, which turns

granular on addition of hydrochloric acid or sal-ammoniac (v. Planta). The previously acid solution is neutral after precipitation with mercuric chloride (Caillot, *Ann. Chim. Phys.* 42, 265). Concentrated alcoholic solutions of mercuric chloride and hydrochlorate of brucine yield small needles, which dissolve when warmed with more alcohol and hydrochloric acid, and are deposited again on cooling (Hinterberger, *Ann. Pharm.* 82, 311).

|  | *at* 100°. |  |  |  | Hinterberger. |
|---|---|---|---|---|---|
| 46 C | 276 | ........ | 39·36 | ........ | 39·31 |
| 2 N | 28 | ........ | 3·99 |  |  |
| 27 H | 27 | ........ | 3·85 | ........ | 4·00 |
| 2 Hg | 200 | ........ | 28·52 | ........ | 27·84 |
| 3 Cl | 106·5 | ........ | 15·16 |  |  |
| 8 O | 64 | ........ | 9·12 |  |  |
| $C^{46}N^2H^{26}O^8,HCl + 2HgCl$ .... | 701·5 | ........ | 100·00 |  |  |

*Terchloride of gold* forms with brucine-salts a brownish-yellow precipitate (Merck). The precipitate is reddish grey-brown, and not perceptibly soluble in hydrochloric acid (v. Planta). It is yellow and amorphous, and perceptible in a solution containing only $\frac{1}{20,000}$th of brucine (Wormley).

*Chloroplatinate of Brucine.* Bichloride of platinum throws down from hydrochlorate of brucine, a dense yellow granular precipitate, not perceptibly soluble in hydrochloric acid (Robinet; v. Planta). The pale-yellow amorphous precipitate thrown down from acetate of brucine quickly becomes crystalline (Wormley). — Yellow crystalline powder, very sparingly soluble in cold water (Liebig). It is decomposed by prolonged boiling with water (Anderson, *Ann. Pharm.* 96, 205).

|  |  |  |  | Liebig. mean. | | Varrentrapp & Will. mean. |
|---|---|---|---|---|---|---|
| $C^{46}N^2H^{26}O^8$ | 394 | ........ | 65·66 |  |  |  |
| $HCl,Cl^2$ | 107·5 | ........ | 17·91 |  |  |  |
| Pt | 98·7 | ........ | 16·43 | ........ | 16·16 | ........ 16·52 |
| $C^{46}N^2H^{26}O^8,HCl,PtCl^2$ .... | 600·2 | ........ | 100·00 |  |  |  |

*Chloride of iridium and sodium* throws down from brucine-salts an ochre-yellow or red-brown precipitate insoluble in hydrochloric acid (v. Planta).

*Hydroferrocyanate of Brucine.* — Shining needles, obtained from ferrocyanide of potassium and nitrate of brucine in the same manner as the corresponding strychnine salt A. (p. 449). Alcoholic hydroferrocyanic acid throws down from alcoholic brucine, an amorphous, white, acid precipitate, resembling the compound B obtained from 1 atom of strychnine and 2 atoms of cyanide of iron. — The needles deposit a blue precipitate when boiled with water (Brandis, *Ann. Pharm.* 66, 266).

| *Needles, dried over chloride of calcium.* |  |  |  | Brandis. mean. |
|---|---|---|---|---|
| 98 C | 588 | ........ | 64·37 | ........ 64·22 |
| 7 N | 98 | ........ | 10·72 |  |
| 56 H | 56 | ........ | 6·11 | ........ 6·52 |
| 18 O | 144 | ........ | 15·74 |  |
| Fe | 28 | ........ | 3·06 |  |
| $2(C^{46}N^2H^{26}O^8,HCy),FeCy + 2HO$ .... | 914 | ........ | 100·00 |  |

*Hydroferricyanate of Brucine.* — Ferricyanide of potassium produces in hydrochlorate of brucine, on standing for some time, crystals which turn blue in a vacuum (Dollfuss). — Dark-yellow salt, resembling in other respects the corresponding strychnine-salt (p. 500) (Brandis).

*Platinohydrocyanate of Brucine.* — Six-sided rhombic tables, obtained from platinocyanide of potassium and brucine-salts (Delffs, *N. Jahrb. Pharm.* 21, 31).

*Hydrosulphocyanate of Brucine.* — Sulphocyanide of potassium throws down from acetate of brucine a white curdy precipitate, which slowly disappears on heating (O. Henry, *J. Pharm.* 24, 149). The precipitate thrown down from hydrochlorate of brucine is granular; nitrate and sulphate of brucine yield laminæ and tables (v. Planta). Sulphocyanide of potassium throws down from dilute hydrochlorate of brucine, tufts of microscopic, very thin needles (Anderson, *N. J. Pharm.* 13, 443). The crystals dissolve easily in pure water, and very easily in alcohol after pouring off the mother-liquor, in which they are nearly insoluble on account of the presence of sulphocyanide of potassium (Lepage, *J. Pharm.* 26, 140). — On neutralising a solution of hydrosulphocyanic acid, not too dilute, with alcoholic brucine, transparent laminæ, are obtained, which do not lose weight or melt at 100°, and are moderately soluble in water (Dollfuss).

|  |  |  |  |  |  | Dollfuss. |
|---|---|---|---|---|---|---|
| 48 C | ............................ | 288 | ........ | 63·57 | ........ | 63·23 |
| 3 N | ............................ | 42 | ........ | 9·27 | | |
| 27 H | ............................ | 27 | ........ | 5·96 | ........ | 6·13 |
| 2 S | ............................ | 32 | ........ | 7·06 | | |
| 8 O | ............................ | 64 | ........ | 14·14 | | |
| $C^{46}N^2H^{26}O^8,C^2NHS^2$ | .... | 453 | ........ | 100·00 | | |

The salt contains 12·90 p. c. of hydrosulphocyanic acid (calc. 13·02 p. c.) (Dollfuss).

*Oxalate of brucine* crystallises in long needles, especially in presence of excess of acid. — *Acetate of brucine* is very easily soluble, and not crystallisable (Pelletier & Caventou). — Neutral *lactate of brucine* dissolves brucine (Coriol, *J. Scienc. Phys.* 3, 247).

*Tartrate of Brucine.* — See p. 216. By dissolving tartaric or antitartaric acid, together with 1 or 2 atoms of brucine, in water or alcohol, four different salts are obtained.

A. *Dextrotartrate of Brucine.* — a. *Semi-acid.* — This salt is immediately deposited, in laminæ, on mixing 2 atoms of alcoholic brucine with 1 atom of alcoholic tartaric acid. The crystals when prepared with 95 p. c. alcohol, contain 11 atoms of water. They lose 9·2 per cent. of water at 100°, and 10 p. c. at 150°, and, therefore, retain 1 atom at 100° (Pasteur).

|  |  |  |  |  |  | Pasteur. |
|---|---|---|---|---|---|---|
| 2 $C^{46}N^2H^{26}O^8$ | ............................ | 788 | ........ | 75·99 | | |
| $C^8H^6O^{12}$ | ............................ | 150 | ........ | 14·46 | | |
| 10 HO | ............................ | 90 | ........ | 8·68 | ........ | 9·20 |
| HO | ............................ | 9 | ........ | 0·87 | ........ | 0·80 |
| 2 $C^{46}N^2H^{26}O^8,C^8H^6O^{12}$ + 11aq. | .... | 1037 | ........ | 100·00 | | |

If in the preparation of this salt the brucine be dissolved in warm aqueous tartaric acid, large transparent crystals with 16 atoms of water are obtained on cooling. These crystals lose 15 atoms of water at 100°, and the remaining atom at 150°, at which temperature they become coloured (Pasteur).

| | | | | | Pasteur. |
|---|---|---|---|---|---|
| $2\ C^{46}N^2H^{26}O^8$ | | 788 | ........ | 72·82 | |
| $C^8H^6O^{12}$ | | 150 | ........ | 13·86 | |
| 15 HO | | 135 | ........ | 12·48 | ........ 12·70 |
| HO | | 9 | ........ | 0·84 | ........ 0·52 |
| $2\ C^{46}N^2H^{26}O^8,C^8H^6O^{12} + 16aq.$ | .... | 1082 | ........ | 100·00 | |

The salt dried at 100° contains 62·99 p. c. C., and 6·84 H. (Pasteur) (by calc. 63·25 p. c. C., 6·29 H.).

b. *Mono-acid.* — This salt is deposited, immediately and completely as a granular crystalline powder, on mixing the alcoholic solutions of brucine and tartaric acid. When crystallised from water, it does not lose water at 100° to 150°, but becomes slightly coloured at 200° (Pasteur).

| | | | | | Pasteur. |
|---|---|---|---|---|---|
| 54 C | | 324 | ........ | 59·55 | ........ 59·83 |
| 2 N | | 28 | ........ | 5·14 | |
| 32 H | | 32 | ........ | 5·88 | ........ 6·19 |
| 20 O | | 160 | ........ | 29·43 | |
| $C^{46}N^2H^{26}O^8,C^8H^6O^{12}$ | ........ | 544 | ........ | 100·00 | |

B. *Antitartrate of Brucine.* — a. *Semi-acid.* — Deposited after some hours, in hard satiny nodules, on mixing solutions of its constituents. It crystallises with the same proportion of water from alcohol of 95 p. c., and from water. Effloresces more easily than the dextrotartrate. Loses 27 atoms of water at 100°, and the last atom at 140° (Pasteur).

| | | | | | Pasteur. |
|---|---|---|---|---|---|
| $2\ C^{46}N^2H^{26}O^8$ | | 788 | ........ | 66·22 | |
| $C^8H^6O^{12}$ | | 150 | ........ | 12·61 | |
| 27 HO | | 243 | ........ | 20·42 | ........ 20·66 |
| HO | | 9 | ........ | 0·75 | ........ 1·03 |
| $2\ C^{46}N^2H^{26}O^8,C^8H^6O^{12} + 28aq.$ | .... | 1190 | ........ | 100·00 | |

b. *Mono-acid.* — Loose silky scales and slender needles, which crystallise with the same proportion of water from 95 p. c. alcohol and from water. The salt effloresces easily. It loses 9 atoms of water at 100°, and the last atom at 150°, evolves an odour of caramel at 190°, and carbonises without melting (Pasteur, *N. Ann. Chim. Phys.* 38, 472).

| | | | | Pasteur. |
|---|---|---|---|---|
| $C^{46}N^2H^{26}O^8$ | | 394 | 62·16 | |
| $C^8H^6O^{12}$ | | 150 | 23·66 | |
| 9 HO | | 81 | 12·77 | ...... 13·30 |
| HO | | 9 | 1·41 | ........ 1·20 |
| $C^{46}N^2H^{26}O^8,C^8H^6O^{12} + 10aq.$ | .... | 634 | 100·00 | |

*Tartrate of Antimony and Brucine.* — Obtained in the same way as the corresponding quinidine-salt (p. 302). — Short brittle crystals (Stenhouse, *Ann. Pharm.* 129, 26).

| | | Crystals. | | | | Stenhouse. |
|---|---|---|---|---|---|---|
| 54 C | .................................... | 324 | ........ | 47·68 | ........ | 48·03 |
| 2 N | .................................... | 28 | ........ | 4·12 | | |
| 31 H | .................................... | 31 | ........ | 4·56 | ........ | 4·64 |
| 22 O | .................................... | 176 | ........ | 25·90 | | |
| Sb | .................................... | 120·3 | ........ | 17·74 | ........ | 17·88 |

$C^{46}N^2H^{26}O^8,HO,SbO^3,C^8H^4O^{10}$ .... 679·3 ........ 100·00

Alcoholic *picric acid* throws down from brucine-salts a yellow or greenish-yellow precipitate, which dissolves with difficulty in hydrochloric, nitric, and acetic acids (Kemp; Wormley, *Repert. Chim. pure* 2, 430; *Chem. News*, 1860, 65). — *Tannic acid, tincture of galls,* and *infusion of galls,* produce dense, dirty-white precipitates, which dissolve in acetic acid (Duflos; Wormley), but not in hydrochloric acid (v. Planta). Tartaric acid prevents the precipitation by tannic acid, but on neutralising the liquid with ammonia a precipitate soluble in excess of ammonia is thrown down (Oppermann). — Brucine behaves in the same manner as quinine (p. 294) towards *oleic acid* and *olive oil* (Attfield).

*Picrotoxin with Brucine.* — On boiling 1 part of brucine with 4 parts of picrotoxin and water, and filtering, the filtrate solidifies to a mass of flexible, opaque, white crystals, which may be recrystallised without change. The compound is decomposed by the electric current, and by alkalis (Pelletier & Couerbe, *Ann. Chim. Phys.* 54, 186).

Brucine dissolves very easily in *alcohol* (Pelletier & Caventou); in 1·5 parts of alcohol (Cap & Garot); easily in cold alcohol of 20° B., and in absolute alcohol (Merck). — It is insoluble in *ether* (Pelletier & Caventou). Dissolves in 1¾ parts (Pettenkofer), in 7 parts of *chloroform* (Schlimpert); in 70 parts of *glycerin* (Cap & Garot); in cold *creosote* and abundantly in warm *picamar* (Reichenbach). — It dissolves very slightly in *volatile oils,* and is insoluble in *fat oils* (Pelletier & Caventou). According to M. Pettenkofer, it dissolves in 56 parts, according to Cap & Garot in 120 parts of fat oil.

*Conjugated Compounds and Derivatives of Brucine.*

## Bromobrucine.

$$C^{46}N^2BrH^{25}O^8 = C^{46}N^2BrH^{23}O^8,H^2.$$
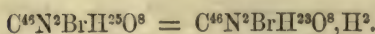
LAURENT. *N. Ann. Chim. Phys.* 24, 314; *Ann. Pharm.* 69, 15; *J. pr. Chem.* 46, 52; *Kopp's Jahresber.* 1847 and 1848, 629.

A solution of bromine in weak spirit is poured into an aqueous solution of sulphate of brucine till ¼th to ⅓rd of the bromine is thrown down as a resin; the supernatant liquid is then mixed with ammonia; the precipitate is dissolved in very weak spirit, and mixed first with boiling water containing a little alcohol, and afterwards with pure water, till cloudiness is produced. The liquid deposits, on cooling, brownish-white needles, which contain 17·5 p.c. of bromine (by calc. 16·91 p.c. Br.), and turn red with nitric acid.

## Methylbrucine.

$$C^{48}N^2H^{28}O^8 = C^{46}N^2(C^2H^3)H^{25}O^8,H^2.$$
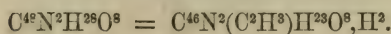
Stahlschmidt. *Pogg.* 108, 535; abstr. *Chem. Centr.* 1860, 216; *Repert. Chim. pure*, 2, 135; *Kopp's Jahresber.* 1859, 398.

*Formebrucin.*—Obtained only in aqueous solution and in combination with acids.

Iodide of methyl converts finely powdered brucine, with liberation of heat, into hydriodate of methylbrucine, from an aqueous solution of which the iodine may be separated by the method described under methylstrychnine (p. 506). The colourless, very bitter solution of *hydrate of methylbrucine* thus obtained, assumes a dark-red colour on standing, more especially when heated, and leaves, when evaporated over oil of vitriol, a brown syrup, which dissolves easily in water, evolves carbonic acid with acids, but does not yield crystallisable salts on account of the partial decomposition of the methylbrucine.

Methylbrucine in the form of sulphate is not poisonous to rabbits in doses of 10 grains.

*Sulphate of Methylbrucine.* — A. *Neutral.* — Radiated crystals, having a bitter taste and easily soluble in water and alcohol, obtained by decomposing hydriodate of methylbrucine with sulphate of silver and evaporating the solution. The crystals lose 13·9 p. c. of water at 130° (8 at. = 13·61 p. c.).

|  | at 130°. |  |  | Stahlschmidt. |
|---|---|---|---|---|
| $C^{48}N^2H^{28}O^8,HO$ ...................... | 417 | ........ | 91·25 |  |
| $SO^3$ ................................ | 40 | ........ | 8·75 | ........ 8·57 |
| $C^{46}N^2H^{25}(C^2H^3)O^8,HO,SO^3$ .... | 457 | ........ | 100·00 |  |

B. *Acid.* — The salt A yields with sulphuric acid indistinct crystals somewhat less easily soluble than A in water and alcohol. — Loses 6·44 p. c. of water at 130° (4 at. = 6·64 p. c.).

|  | Dried. |  |  | Stahlschmidt. |
|---|---|---|---|---|
| $C^{48}N^2H^{28}O^8,2HO$ .......................... | 426 | ........ | 84·19 |  |
| $2 SO^3$ ................................ | 80 | ........ | 15·81 | ........ 15·97 |
| $C^{46}N^2H^{25}(C^2H^3)O^8,2(HO,SO^3)$ .... | 506 | ........ | 100·00 |  |

*Hydriodate of Methylbrucine.* — Dissolves in hot water more easily than the corresponding salt of methyl-strychnine, and crystallises in small shining laminæ on cooling. The crystals lose 21·47 p. c. of water over the water-bath (16 at. = 21·2 p. c. HO).

|  | Dried. |  |  | Stahlschmidt. |
|---|---|---|---|---|
| $C^{46}N^2H^{28}O^8,H$ ............... | 409 | ........ | 76·30 |  |
| $I$ ...................... | 127 | ........ | 23·70 | ........ 24·22 |
| $C^{46}N^2H^{25}(C^2H^3)O^8,HI$ .... | 536 | ........ | 100·00 |  |

*Hydrobromate of Methylbrucine.* — Bromide of potassium throws down from hydrochlorate of brucine, on standing for some time, a

crystalline precipitate which crystallises from hot water in small shining prisms. — The salt dissolves easily in water and alcohol. — Loses 8·5 p. c. of water at 130° (5 at. = 8·4 p. c. HO).

| | Dried. | | Stahlschmidt. |
|---|---|---|---|
| $C^{48}N^2H^{28}O^8,H$ .................... | 409 | ........ 83·64 | |
| Br................................ | 80 | ........ 16·36 | ........ 15·74 |
| $C^{46}N^2H^{25}(C^2H^3)O^8,HBr$ .... | 489 | ........ 100·00 | |

*Hydrochlorate of Methylbrucine.* — Small shining crystals, easily soluble in water and in alcohol. — Loses 16·6 p. c. of water over the water-bath (10 at. = 16·8 p. c. HO).

| | Dried. | | Stahlschmidt. |
|---|---|---|---|
| $C^{48}N^2H^{28}O^8,H$ .................... | 409 | ... .... 92·01 | |
| Cl................................ | 35·5 | ........ 7·99 | ........ 8·15 |
| $C^{46}N^2H^{25}(C^2H^3)O^8,HCl$ .... | 444·5 | ........ 100·00 | |

*Mercuric chloride* throws down from hydrochlorate of methylbrucine a white curdy precipitate, soluble in water and alcohol, but insoluble in ether.

*Chloroplatinate of Methylbrucine.* — Yellow precipitate crystallising from water in fine needles, easily soluble in water and alcohol, insoluble in ether. Contains, at 100°, 16·35 p. c. of platinum (calc. 16·07 p. c.).

*Chloroaurate of Methylbrucine.* — Orange-yellow precipitate, which crystallises from a solution in hot water. It is decomposed by long boiling, with separation of gold. Dissolves with difficulty in cold water, easily in hot water and hot alcohol. — Contains, after drying at 100°, 26·47 p. c. of gold (calc. 26·34 p. c.).

# Ethylbrucine.

$$C^{50}N^2H^{30}O^8 = C^{46}N^2(C^4H^5)H^{23}O^8,H^2.$$
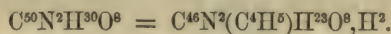
GUNNING. *J. pr. Chem.* 67, 46; *Kopp's Jahresber.* 1856, 546.

*Vinebrucin.*—Known only in combination with water and acids.

Hydriodate of ethyl-brucine, obtained by mixing alcoholic brucine with iodide of ethyl, yields, when digested with oxide of silver, iodide of silver and *hydrate of ethylbrucine,* the latter as a strongly alkaline liquid which becomes coloured and absorbs carbonic acid when evaporated. It decomposes ammonia-salts with liberation of ammonia, and the salts of iron, alumina, and zinc, precipitating the hydrates, and redissolving those of alumina and zinc. It reddens nitric acid like brucine.

*Hydriodate of Ethylbrucine.* — Crystallises from a mixture of alcoholic brucine and iodide of ethyl on standing for some time. It is not decomposed by caustic potash. — Dissolves with moderate facility in hot alcohol. The salt dried at 100° loses 1·65 p. c. of water at 140° (1 at. = 1·6 p. c.).

| | | at 100°. | | | | Gunning. mean. |
|---|---|---|---|---|---|---|
| 50 C | .................................. | 300 | ........ | 53·67 | ........ | 53·25 |
| 2 N | .................................. | 28 | ........ | 5·01 | ........ | 4·70 |
| 32 H | .................................. | 32 | ........ | 5·72 | ........ | 5·90 |
| 9 O | .................................. | 72 | ........ | 12·88 | ........ | 13·27 |
| I | .................................. | 127 | ........ | 22·72 | ........ | 22·88 |
| $C^{46}N^2(C^4H^5)H^{25}O^3,HI + HO$ | .... | 559 | ........ | 100·00 | ........ | 100·00 |

*Chloroplatinate of Ethylbrucine.* — Golden-yellow precipitate, crystallising from boiling water.

| | | | | Gunning. |
|---|---|---|---|---|
| $C^{50}N^2H^{30}O^3,HCl,Cl^2$ | ................... | 529·5 | ........ | 84·27 |
| Pt | ................................ | 98·7 | ........ | 15·73 | ........ | 15·20 |
| $C^{46}N(C^4H^5)H^{25}O^8,HCl,PtCl^2$ | .... | 628·2 | ........ | 100·00 |

## Compounds obtained from Brucine and Bibromide of Ethylene.

L. SCHAD. *Ann. Pharm.* 118, 207; *J. pr. Chem.* 84, 248; *Chem. Centr.* 1861, 908; *Repert. Chim. pure* 4, 46; *Kopp's Jahresber.* 1861, 542.

Powdered brucine is but slightly attacked by bibromide of ethylene at ordinary temperatures, but dissolves rapidly at 100°, forming a transparent colourless liquid, which solidifies in a crystalline mass on cooling. The crystals may be freed from excess of the bibromide by recrystallisation from boiling water.

The inodorous pearly laminæ thus obtained are Schad's hydrated *Bihydrobromate of Ethylene-brucine* or *Bromide of Brucine-bromethylene-ammonium.* They dissolve easily in hot water, with difficulty in absolute alcohol, and are insoluble in ether. The aqueous solution is not precipitated by ammonia or alkalis. — The crystals lose 8·56 p. c. water at 100° (6 at. = 8·49 p. c.).

| | | Dried. | | | | Schad. mean. |
|---|---|---|---|---|---|---|
| 50 C | .................................. | 300 | ........ | 51·54 | ........ | 51·45 |
| 2 N | .................................. | 28 | ........ | 4·80 | | |
| 30 H | .................................. | 30 | ........ | 5·15 | ........ | 5·27 |
| 8 O | .................................. | 64 | ........ | 10·99 | | |
| 2 Br | .................................. | 160 | ........ | 27·52 | ........ | 25·82 |
| $C^{46}N^2H^{24}(C^4H^4)O^8,2HBr$ | .... | 582 | ........ | 100·00 | | |

In contact with silver-salts, the crystals give up half their bromine, and when heated, the whole of the bromine, as bromide of silver, thus forming two series of compounds corresponding in every respect to those obtained in the same way with strychnine (p. 513).

A. *Compound containing Bromine.* — When the crystals are decomposed with nitrate of silver, and the filtrate, freed from excess of silver by hydrochloric acid, is precipitated with bichloride of platinum, yellow flocks are obtained, which quickly turn crystalline, and contain 13·84 p. c. of platinum. The flocks are represented by the formula $C^{46}N^2H^{25}(C^4H^4Br)O^8,HCl,PtCl^2$ (calc. 13·95 p. c. Pt).

B. *Hydrate of Ethylene-brucine free from Bromine.* [*Brucinvinyl-Ammoniumoxydhydrat* (Schad)]. Obtained by digesting the warm aqueous solution of the above crystals with freshly precipitated oxide of silver, and evaporating the strongly alkaline filtrate, which takes up carbonic acid from the air. There remains a brown viscid varnish, which neutralises acids, forming salts.

*Sulphate.* — *Acid.* — Large transparent crystals which effloresce and decompose in the air. They lose 3·11 p. c. of water at 100° and the remainder (amounting altogether to 9·35 p. c.) at 130° (2 and 6 at. = 3·1 and 9·4 p.c. HO).

| | | at 100°. | | | | Schad. |
|---|---|---|---|---|---|---|
| 50 C | ......... | 300 | ........ | 54·15 | ........ | 54·23 |
| 2 N | ......... | 28 | ........ | 5·06 | | |
| 34 H | ......... | 34 | ........ | 6·14 | ........ | 6·40 |
| 14 O | ......... | 112 | ........ | 20·21 | | |
| 2 SO³ | ......... | 80 | ........ | 14·44 | ........ | 14·44 |

$C^{46}N^2H^{24}(C^4H^4)O^3,2(HO,SO^3) + 4aq.$ .... 554 ........ 100·00

*Chloroplatinate.* — Pale lemon-yellow precipitate thrown down from the hydrochlorate by bichloride of platinum.

| | | | | | | Schad. mean. |
|---|---|---|---|---|---|---|
| 50 C | ......... | 300 | ........ | 47·90 | ........ | 47·91 |
| 2 N | ......... | 28 | ........ | 4·47 | | |
| 29 H | ......... | 29 | ........ | 4·63 | ........ | 4·75 |
| 8 O | ......... | 64 | ........ | 10·22 | | |
| Pt | ......... | 98·7 | ........ | 15·76 | ........ | 15·63 |
| 3 Cl | ......... | 106·5 | ........ | 17·02 | | |

$C^{46}N^2H^{24}(C^4H^4)O^3,HCl,PtCl^2$ .... 626·2 ........ 100·00

*Appendix to Brucine.*

# 1. Igasurine.

Desnoix. *N. J. Pharm.* 25, 202; *Pharm. Centr.* 1854, 654; *Pharm. Viertelj.* 4, 94. *Kopp's Jahresber.* 1854, 524.

Schützenberger. *Compt. rend.* 46, 1234; *Instit.* 1858, 217; *N. J. Pharm.* 35, 31; *Rép. Chim. pure,* 1, 76; *J. pr. Chem.* 74, 510; *Chem. Centr.* 1858, 557; *Chem. Gaz.* 1858, 467; *Ann. Pharm.* 108, 348; Complete: *N. Ann. Chim. Phys.* 54, 65; *Kopp's Jahresber.* 1858, 374.

Occurs in *Nux vomica,* and remains in solution after the strychnine and brucine have been precipitated from the boiling extracts by lime. The filtrate, when concentrated and left at rest for some days, deposits crystals of igasurine, which are to be dissolved in hydrochloric acid, decolorized with animal charcoal, and precipitated by ammonia, afterwards crystallised from alcohol and purified by again dissolving them in hydrochloric acid and precipitating with ammonia. On agitating the ammonia-precipitate with the mother-liquor, it takes up water and becomes crystalline.

The crystals, which contain 10 p. c. water, form feathery groups of white silky needles having a very bitter taste and a poisonous action.    They resemble brucine in their behaviour towards reagents, and rotate a polarised ray of light in the same direction and to nearly the same extent : they differ from brucine, however, in being precipitated by bicarbonate of potash, even in presence of tartaric acid ; moreover they are soluble in 200 parts of boiling water, from which they crystallise very rapidly in cooling, whereas brucine dissolves only in 500 parts of boiling water and crystallises slowly (Desnoix).

Igasurine behaves towards oleic acid and olive oil in the same way as quinine (p. 294) (Attfield).

Crystals prepared as above or by concentrating the mother-liquors of strychnine, and occurring in commerce as brucine, are according to Schützenberger, a mixture of different bases, of which he found in one sample as many as five.

A. *First Sample.* — This specimen formed a mixture of very long and short needles, separable into five bases, the whole of which were very bitter, poisonous, assumed a red colour with nitric acid like brucine, dissolved in alcohol much more easily than in ether, and formed easily crystallisable salts.

On boiling this specimen with water, a portion dissolved, whilst the remainder melted to a semi-fluid resin which dissolved only on boiling with a very large quantity of water.    The latter solution deposited the whole of the dissolved matter, on cooling, in very large scales, which were formed of long pearly needles, and retained their form when recrystallised :—*a*-igasurine.—The solution formed by the first boiling with water, decanted at the boiling heat, deposited three bases in succession on cooling ; *b*-igasurine in separate needles at 85° ; *c*-igasurine at 45° ; and *d*-igasurine slowly in scales at 30° : from the mother-liquor, which deposited no more crystals, bichloride of platinum threw down *e*-igasurine as platinum-salt.

*a-Igasurine.*  $C^{44}N^2H^{26}O^8$.    Loses 13·2 p. c. of water at 130° (6 at. = 12·38 p. c. HO).    The platinum-salt contains 16·6 p. c. of platinum (by calc. 16·78 p. c. Pt). — Very slightly soluble in water.

*b-Igasurine.*  $C^{36}N^2H^{40}O^{14}$.    Loses 12·7 p. c. of water at 130° (6 at. = 12·44 p. c. HO).    The platinum-salt contains 16·79 p. c. of platinum (by calc. 16·84 p. c. Pt). — Slightly soluble.

*c-Igasurine.*  $C^{36}N^2H^{24}O^8$.    Loses 14·06 p. c. of water at 130° (6 at. = 13·98 p. c. HO).    The platinum-salt contains 18·2 p. c. of platinum (by calc. 18·32 p. c. Pt). — Soluble.

*d-Igasurine.*  $C^{34}N^2H^{32}O^{16}$.    Loses 11·7 p. c. of water at 130° (6 at. = 12·11 p. c. HO). — Soluble.

*e-Igasurine.*  $C^{36}N^2H^{28}O^8$.    The platinum-salt, $C^{36}N^2H^{26}O^8,HCl,PtCl^2$, contains 39·7 p. c. C., 5·1 H., and 18·52 Pt (calc. 39·98 p. c. C., 4·81 H., 18·27 Pt). — Easily soluble.

Analyses by Schützenberger.
Dried at 130°.

| | | a. | | b. | | c. | | d. |
|---|---|---|---|---|---|---|---|---|
| C | ........ | 68·78 | ........ | 56·84 | ........ | 64·87 | ........ | 52·2 |
| N | ........ | 7·05 | ........ | 7·19 | ........ | 8·00 | ........ | 7·3 |
| H | ........ | 6·94 | ........ | 6·54 | ........ | 7·20 | ........ | 8·5 |
| O | ........ | 17·23 | ........ | 29·43 | ........ | 19·93 | ........ | 32·0 |
| | | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·0 |

Calculations.

| a. | | b. | | c. | | d. | |
|---|---|---|---|---|---|---|---|
| 44 C .... | 69·11 | 36 C .... | 56·86 | 36 C .... | 65·06 | 34 C .... | 52·04 |
| 2 N .... | 7·33 | 2 N .... | 7·36 | 2 N .... | 8·43 | 2 N .... | 7·14 |
| 26 H .... | 6·83 | 24 H .... | 6·31 | 24 H .... | 7·23 | 32 H .... | 8·16 |
| 8 O .... | 16·73 | 14 O .... | 29·47 | 8 O .... | 19·28 | 16 O .... | 32·66 |
| $C^{44}N^2H^{26}O^8$ | | $C^{36}N^2H^{24}O^{14}$ | | $C^{36}N^2H^{24}O^8$ | | $C^{34}N^2H^{32}O^{16}$ | |

B. *Second Sample.* — This specimen contained only one base, which resembled *e*-igasurine in point of solubility, and, like it, formed separate needles. Loses 14·4 p. c. of water at 130° (6 and 8 at. = 12·61 and 16·14 p. c. HO). — With nitrous acid it forms oxyigasurine.

| | *f-Igasurine.* | | | | Schützenberzer. at 130° |
|---|---|---|---|---|---|
| 42 C ................ | 252 | ........ | 67·38 | ........ | 67·22 |
| 2 N ................ | 28 | ........ | 7·48 | ........ | 7·20 |
| 30 H ................ | 30 | ........ | 8·02 | ........ | 7·99 |
| 8 O ................ | 64 | ........ | 17·12 | ........ | 17·59 |
| $C^{42}N^2H^{30}O^8$ .... | 374 | ........ | 100·00 | ........ | 100·00 |

C. *Third Sample.* — On dissolving the sulphate of this specimen in boiling water, and mixing the solution at 75° with ammonia, *g*-igasurine was deposited as a fluid resin, after the removal of which, *h*-igasurine crystallised in needles, and subsequently *i*-igasurine in silky needles.

*g-Igasurine.* $C^{42}N^2H^{28}O^{12}$. Solidifies rapidly, and is obtained from alcohol, in loose crystals, or on addition of water, in which it dissolves very slightly, in scales. Loses 11·5 p. c. of water at 130° (6 at. = 11·79 p. c.). The platinum-salt contains 15·9 to 16·1 p. c. platinum (calc. 16·17 p. c. Pt.).

*h-Igasurine.* $C^{42}N^2H^{26}O^{12}$. Loses 7·5 p. c. of water at 130° (4 at. = 8·22 p. c.). More easily soluble than *g*.

*i-Igasurine.* $C^{40}N^2H^{26}O^{14}$. Loses 14·56 p. c. of water at 130° (8 at. = 15·04 p. c.). The platinum-salt contains 15·7 p. c. platinum (calc. 16·12 p. c. Pt.). — Soluble.

According to Schützenberzer, at 130°.

| g. | Sch. | h. | Sch. | i. | Sch. |
|---|---|---|---|---|---|
| 42 C ...... 62·37.. | 62·20 | 42 C ...... 62·68..62·4 | | 40 C ...... 59·11.. | 58·90 |
| 2 N ...... 6·93.. | 6·90 | 2 N ...... 6·97 | | 2 N ...... 6·90.. | 6·80 |
| 28 H ...... 6·93.. | 6·75 | 26 H ...... 6·47.. 6·6 | | 26 H ...... 6·40.. | 6·49 |
| 12 O ...... 23·77.. | 24·15 | 12 O ...... 23·88 | | 14 O ...... 27·59.. | 27·81 |

$C^{42}N^2H^{28}O^{12}$ 100·00..100·00    $C^{42}N^2H^{26}O^{12}$ 100·00    $C^{40}N^2H^{26}O^{14}$ 100·00..100·00

## Oxyigasurine.

Schützenberger. *N. Ann. Chim. Phys.* 54, 65.

On heating an aqueous solution of sulphate of *f*-igasurine to boiling with nitrite of potash, an effervescence takes place, and oxygasurine is formed. The product is rather more soluble in water than igasurine, and crystallises from the solution in isolated translucent needles after 12 hours only.

The needles melt in their water of crystallisation at 100°, and lose 13·4 p. c. of water at 130° (8 at. = 13·68 p. c. HO). — The platinum-salt contains 14·6 p. c. platinum (calc. 14·95 p. c.)

|  | | at 130°. | | | Schützenberger. |
|---|---|---|---|---|---|
| 42 C | .................. | 252 | ........ | 55·51 | ........ | 55·66 |
| 2 N | .................. | 28 | ........ | 6·17 | ........ | 6·30 |
| 30 H | .................. | 30 | ........ | 6·61 | ........ | 6·74 |
| 18 O | .................. | 144 | ........ | 31·71 | ........ | 31·30 |
| $C^{42}N^2H^{30}O^{18}$ | .... | 454 | ........ | 100·00 | ...... | 100·00 |

## 2. Curarine.

$$C^{20}NH^{15} = C^{20}NH^{13},H^2.$$
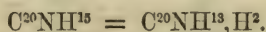
Roulin & Boussingault. *Ann. Chim. Phys.* 39, 24; abstr. *J. Chim. méd.* 4, 71; *Berz. Jahresber.* 9, 220.
Pelletier & Petroz. *Ann. Chim. Phys.* 40, 213; *N. Tr.* 19, 2, 107; *Br. Arch.* 30, 288.
A. Buchner. *N. Repert.* 10, 167; *N. Br. Arch.* 110, 19; *Kopp's Jahresber.* 1861, 767.
W. Preyer. *Zeitschr. Ch. Pharm.* 8, 381; *N. J. Pharm.* [4], 2, 296; *Compt. rend.* 60, 1346.

Discovered by Buchner, sen. (*Toxikologie*, 1827, 249), and afterwards, in 1828, by Roulin and Boussingault, and prepared pure by Preyer. — Occurs in the arrow-poison of the Indians of the Upper Orinoco, which is known as *Curare* or *Urari*, and is obtained from the sap of some species of *Strychnos*. According to Henkel (*N. Repert.* 10, 164), however, the following varieties are to be distinguished:—

a. *Curare* from *Guiana*, the arrow-poison containing curarine, occurring in earthern vessels, and prepared from *Rouhamon guianensis* and *Strychnos cogens*.

b. *Urari* from *Strychnos toxifera* (*Schomburgh*), occurring in cala-bashes. This substance is said not to contain any active constituent which can be isolated.

c. East Indian arrow-poison containing strychnine, *Upas radja* or *Tienté*.

According to A. Buchner, the distinction between *a* and *b* is unfounded, the curare of the Indians of the Upper Orinoco being essentially identical with the Urari of the Rio Yupura and Rio Negro, as well as with the *Wurali* of Surinam, in support of which view Buchner cites the experiments of Pelikan & Trapp. Milleroux (*Compt. rend.* 47, 973) appears to hold the same opinion. Von Martius described as Urari an arrow-poison in earthen vessels brought by him from Northern Brazil in 1821. This substance was employed in Buchner's and (as curare) in Henkel's experiments, also in those of Wittstein (*Pharm. Viertelj.* 8, 402; *N. Br. Arch.* 100, 129), who supposed it to contain strychnine and brucine. This last supposition was contradicted by Wittstein's own experiments, and was also shown to be erroneous by Buchner and Henkel.

The bark of *Strychnos toxifera* appears, from the experiments of Wittstein, to contain curarine. — Preyer found curarine in the fruit of *Paullinia curare*, and it is probable that curare is obtained from this fruit.

*Curare* is obtained by exhausting the sap and bark of a species of Strychnos with cold water, and evaporating the extract, together with another very viscid vegetable extract. It forms a nearly black hygroscopic extract, very bitter, soluble for the most part in water, and contains, besides curarine, fat, brown resin, red colouring matter, gum, and clay (Boussingault & Roulin). See also Pelletier and Petroz. It is not poisonous when taken internally in small quantities, but quickly produces death when introduced into wounds (Humboldt, *Ann. Chim. Phys.* 39, 30).

*Preparation of Curarine.* Powdered curare is boiled with absolute alcohol and a few drops of caustic soda; the tincture is freed from alcohol by distillation, and the residue is mixed with water, which throws down resin. The solution, filtered from resin, is precipitated by phosphomolybdic acid, and the precipitate is decomposed by drying with hydrate of baryta, and afterwards exhausted with absolute alcohol. From the solution thus obtained, anhydrous ether throws down white flocks, which rapidly deliquesce to a brown oil in the air, and rarely crystallise from water, but may be obtained in crystals by dissolving them in chloroform and evaporating the solution. — Or the curarine may be obtained as hydrochlorate by precipitating the solution freed from resin with mercuric or platinic chloride, decomposing the precipitate by hydrosulphuric acid, and repeating this process (Preyer).

Roulin & Boussingault dissolve the alcoholic extract of curare in water, filter from resin, decolorise the solution with animal charcoal, precipitate with infusion of galls, dissolve the yellowish-white precipitate, after washing, in boiling water containing oxalic acid, boil the solution with magnesia, evaporate the filtrate, exhaust the residue with alcohol, and evaporate. Curarine then remains as a pale yellow syrup, drying up over oil of vitriol to a horny very bitter mass, which turns turmeric red and litmus blue. — Buchner jun., precipitates the aqueous extract of curare with neutral acetate of lead, frees the filtrate from lead by hydrosulphuric acid, and evaporates to a syrup, which he agitates with soda-ley and chloroform. On evaporating the chloroform, curarine remains as an amorphous brown mass.

*Properties.* Colourless four-sided prisms having a slightly alkaline reaction, very hygroscopic and very bitter (Preyer). Tastes bitter, though less persistently so than strychnine (Buchner). Much more poisonous than curare; paralyses the extremities and produces death without convulsions (Buchner). See also Bernard (*N. J. Pharm.* [4] 2, 165).

*Decompositions.* Curarine, when *heated*, evolves ammoniacal bitter vapours, and a horny odour. — It assumes with *oil of vitriol* a fine blue (Preyer), a carmine-red colour (Roulin & Boussingault). — Strong *nitric acid* produces a purple-red (Preyer), a blood-red colour (Roulin & Boussingault). — When mixed with oil of vitriol, and afterwards with *bichromate of potash*, curarine assumes a violet colour in the same manner as strychnine, but the colour, and likewise that produced by oil of vitriol, is more stable with curarine (Preyer). With curare or impure curarine, Henkel obtained a brown colour, passing into cherry-red and violet. *Peroxide of lead* or *ferricyanide of potassium* and oil of vitriol, likewise produce the violet colour.

*Combinations.* Curarine deliquesces in the air, and dissolves in *water* in all proportions (Preyer; Roulin & Boussingault). — It forms with *acids* neutral, very easily soluble salts, which turn brown when warmed. The nitrate, sulphate, hydrochlorate, and acetate crystallise; the crystalline *platinum-salt* is thrown down from curarine free from hydrochloric acid by bichloride of platinum, and corresponds to the formula C²⁰NH¹⁵,PtCl² (Preyer).

Curarine dissolves in all proportions in *alcohol*, and slightly in anhydrous *ether, sulphide of carbon, oil of turpentine,* and *benzene* (Preyer). Infusion of galls throws down from the aqueous solution a precipitate soluble in alcohol (Pelletier & Petroz).

## 3. Conessine or Wrightine.

HAINES.   *Verhandl. der medic.-physik. Gesellschaft von Bombay* 1858;
➤   *Schweiz. Pharm. Wochenschr.* 1865, 172.
STENHOUSE.   *Pharm. J. Trans.* 1864, 5, 493; *Pharm. Viertelj.* 14, 301;
   *Schweiz. Pharm. Wochenschr.* 1865, 172.

*Neriine.* Occurs in the seeds of *Wrightia antidysenterica*, an East Indian apocynaceous plant, the *Semen Indageer* of the druggists (Stenhouse), the extract of which has, according to Husemann, a narcotic action. It occurs in the bark of the same plant, the Kuda bark of the bazaars, to the amount of $\frac{1}{10}$th per cent. (Haines).

*Preparation.* 1. *From the seeds.* The fatty oil of the seeds is removed by means of bisulphide of carbon; the residue is digested with alcohol; the extract is filtered and freed from alcohol by distillation; the residual mass is exhausted with dilute hydrochloric acid; and the filtrate is precipitated by ammonia. The flocks thus obtained are purified by washing with cold water (Stenhouse). — 2. *From the*

*bark*. The extract prepared with dilute hydrochloric acid is precipi-
tated by ammonia; the precipitate is exhausted with alcohol, and the
tincture is evaporated to a syrup, which is evaporated to dryness with
neutral acetate of lead and a little ammonia, and afterwards exhausted
with ether. On evaporating the ether, conessine remains as an amor-
phous brown-yellow resin, which softens at 71°, and melts below 100°
(Haines).

*Properties.* White amorphous powder, having a very bitter (Sten-
house) and also acrid and harsh taste (Haines). Contains 78·3 p. c. C.,
11·2 H.; the conessine in the platinum-salt contained 77·3 p. c. C.,
11·8 H., and 7·73 N., from which numbers Haines calculated the
formula $C^{26}NH^{20}O$.

Conessine decomposes when *heated.* — With *nitric acid* it forms
oxalic but no picric acid. — It dissolves slightly in boiling *water*, and
easily in dilute acids, forming amorphous salts. The solution in hydro-
chloric acid yields a flocculent precipitate with *mercuric chloride, chloride
of gold*, and *chloride of platinum* (Stenhouse). The amorphous yellow
flocks of the platinum-salt contain 24·05 to 25·06 p. c. of platinum
(Haines). *Tannic acid* throws down from acetate of conessine, flocks
soluble in hydrochloric acid (Stenhouse).

! Conessine dissolves in *alcohol, ether*, and *chloroform* (Haines).
According to Stenhouse, it is slightly soluble in boiling alcohol, but
nearly insoluble in ether and *bisulphide of carbon.*

# 4. Eserine.

JOBST & HESSE. *Ann. Pharm.* 129, 115; *N. Repert.* 13, 80.
AM. VEE & LEVEN. *N. J. Pharm.* [4] 1, 70; *Compt. rend.* 60, 1194;
  *N. Repert.* 14, 75.

*Physostigmine.*—Occurs in the cotyledons (Jobst and Hesse) of the tasteless
poisonous Calabar bean of *Physostigma venenosum*, concerning which see Henkel
(*N. Jahrb. Pharm.* 21, 1). On poisoning by calabar beans and the detection of the
poison, see Edwards (*N. Repert.* 14, 79; *Chem. Centr.* 1865, 647).

*Preparation.* 1. The powdered beans are exhausted with cold
alcohol of 95 p. c.; the tincture is distilled; and the extract is digested
with a strong aqueous solution of tartaric acid. The solution thus
obtained is diluted with water, filtered, supersaturated with bicarbonate
of potash, and again filtered, and the filtrate is shaken up with ether
so long as it gives up eserine. The residue which remains on evapo-
rating the ether is dried over oil of vitriol and exhausted with absolute
ether, which leaves eserine on evaporation. The product is purified
by crystallisation from alcohol and ether, but cannot be completely
freed from red colouring matter (Vee & Leven). — 2. Jobst and Hesse
exhaust the beans with hot alcohol, dissolve the extract in water,
acidify the solution, and precipitate with neutral acetate of lead.
After removing this precipitate, the filtrate is freed from lead by hydro-
sulphuric acid, and evaporated over a water-bath, and the residual
extract is treated with absolute alcohol, which takes up acetate of

eserine, leaving gum undissolved. A solution of the acetate in cold water, when shaken with magnesia and ether, gives up to the latter liquid the eserine, together with fat and colouring matter, to remove which the decanted ethereal layer is shaken with dilute sulphuric acid, whereupon the eserine becomes dissolved in the aqueous liquid as sulphate, the fat remaining in the ether. The aqueous solution is separated, decomposed by magnesia, and freed from eserine by agitation with ether, which leaves it, on evaporation, as a brown-yellow amorphous mass (Jobst & Hesse).

*Properties.* Very thin, rhombic laminæ, truncated at the obtuse angles (Vee & Leven). Its aqueous solution has a slightly burning taste and a distinctly alkaline reaction. It is extremely poisonous, producing paralysis of the muscles, loss of motion, and death. Its aqueous solution, introduced into the eye, produces contraction of the pupil, even an hour after the death of the animal (Jobst & Hesse). — Contains nitrogen. — Melts on platinum-foil, emitting a large quantity of white fumes.

Eserine dissolves very slightly in *water* (Vee & Leven), more easily in aqueous *ammonia*, and in *caustic soda* or its *carbonate*. — *Biniodide of potassium* throws down from aqueous eserine, a carmine-coloured precipitate (Jobst & Hesse).

Eserine dissolves in acids, forming soluble salts, red and amorphous (according to Jobst & Hesse), the solutions of which are decolorised by hydrosulphuric acid. Aqueous eserine throws down sesquioxide of iron from the sesquichloride.

*Mercuric chloride* throws down from hydrochlorate of eserine, a reddish-white amorphous precipitate, easily soluble in hydrochloric acid, but not in an aqueous solution of the precipitant. *Bichloride of platinum* produces a pale-yellow amorphous precipitate, soluble in hydrochloric acid and in boiling water, and decomposible by an excess of hot bichloride of platinum. *Terchloride of gold* produces a bluish precipitate, with separation of gold. *Tannic acid* throws down amorphous, reddish-white flocks, soluble in a large quantity of hydrochloric acid (Jobst & Hesse).

Eserine dissolves easily in *alcohol, ether, chloroform*, and *benzene*. It is thrown down from the ethereal solution by *animal charcoal*.


## 5. Oleandrine and Pseudocurarine.

From *Nerium Oleander*, from which plant Landerer (*Repert.* 71, 247) obtained resins, Lucas (*N. Br. Arch.* 97, 149) a white powder, soluble in acids and precipitable by tannic acid. — An aqueous extract of the leaves is precipitated with tannic acid; the precipitate is washed with cold water; and the pseudocurarine is extracted from it by treatment with aqueous tannic acid. The solution is boiled with oxide of lead, filtered, evaporated to a syrup, and exhausted with ether, which takes up a little oleandrine, after which the residue gives up pseudocurarine to alcohol. — The tannate of oleandrine may be freed from adhering leaf-green by ether.

*Pseudocurarine* is not volatile and not poisonous. It dissolves in

water and alcohol, but not in ether. It neutralises acids, forming amorphous salts, and precipitates mercuric chloride and bichloride of platinum. — *Oleandrine* is yellow, amorphous, poisonous, and very bitter. It dissolves very slightly in water, but more freely in alcohol and ether. It combines with acids, and precipitates solutions of gold and platinum (Leukowsky, *N. J. Pharm.* 46, 397).

*Primary Nucleus* $C^{46}H^{46}$; *Oxyazo-nucleus* $C^{46}NH^{27}O^{18}$.

## Narceine.

$$C^{46}NH^{29}O^{18} = C^{46}NH^{27}O^{18},H^2.$$
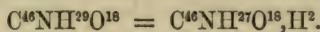
PELLETIER. *Ann. Chim. Phys.* 50, 252, and 262; *J. Pharm.* 18, 607, and 616; *Ann. Pharm.* 5, 163; *Schw.* 67, 311; abstr. *Pogg.* 27, 659. — *J. Pharm.* 21, 573; *Ann. Pharm.* 16, 47; *N. Br. Arch.* 5, 158.
COUERBE. *Ann. Chim. Phys.* 59, 151; *Ann. Pharm.* 17, 171.
WINCKLER. *Repert.* 59, 1.
ANDERSON. *Trans. Roy. Soc. Edin.* 20, 3, 347; *Chem. Soc. Qu. J.*, 5, 257; *Ann. Pharm.* 86, 182; *J. pr. Chem.* 57, 358; *Kopp's Jahresber.* 1852, 537.
O. HESSE. *Ann. Pharm.* 129, 250; *N. Repert.* 13, 83.

Discovered by Pelletier in 1832 (*J. Pharm.* 18, 150; *Ann. Pharm.* 2, 274).

*Source.* In opium. — Also in the ripe capsules of the blue-seeded poppy (Winckler). — Couerbe obtained 6 drams of narceine from 40 pounds of opium.

*Preparation.* Narceine is obtained in the treatment of opium, described at pp. 419—422, vol. xvi. It remains in the filtrate, from which the greater part of the morphine has been precipitated by ammonia, and crystallises therefrom after the separation of the meconic acid and excess of baryta. — If the filtrate be neutralised with hydrochloric acid, and evaporated to crystallisation, a part of the narceine crystallises out, while another portion remains in the mother-liquor. On dissolving about $\frac{9}{10}$ths of the crystals in water, narceine chiefly remains undissolved, and may be purified by recrystallisation from boiling water. A further portion may also be obtained from the filtrate (Pelletier).

See Anderson's method, xvi, 240. The product is still to be purified by recrystallisation from a large quantity of boiling water, dissolving in alcohol, boiling with animal charcoal, and again dissolving in water. When narceine containing morphine is dissolved in a nearly boiling solution of very weak caustic potash, and the filtrate is mixed with acetic acid to slight acid reaction, the narceine crystallises out, whilst the morphine remains in solution as acetate (Pelletier). Narceine and meconin may be separated by means of ether, which dissolves only the latter.

*From the ripe capsules of the Blue-seeded Poppy.* The extract prepared with boiling alcohol of 80 p. c., when dissolved in boiling water, leaves behind light-brown flocks of impure narceine, more of which may be obtained by evaporating the filtrate, and diluting with water; also by again evaporating the filtrate to an extract, and leaving it to stand; the narceine is then deposited. The deposits are purified by repeated crystallisation from boiling alcohol, with help of animal charcoal (Winckler).

*Properties.* Narceine is obtained in hydrated crystals which give up their water with difficulty at 100° (Anderson). Tufts of white silky needles [or long four-sided right rhombic prisms (Pelletier, *Ann. Chim. Phys.* 53, 431)]. Inodorous. Tastes slightly bitter at first, and afterwards peculiarly styptic (Winckler). Melts at 145·2° (Hesse), 92° (Pelletier) and solidifies to a translucent amorphous mass on cooling. — Rotates a ray of polarised light to the left; $[\alpha] r = 66·7°$ (Bouchardat & Boudet, *N. J. Pharm.* 23, 292).

|  |  | at 110°. |  | Pelletier. | Couerbe. | Anderson. | Hesse. |
|---|---|---|---|---|---|---|---|
| 46 C | ............... | 276 | .... | 59·63 | 54·02 | 56·21 | 59·34 .... 59·29 |
| N | ............... | 14 | .... | 3·02 | 4·33 | 4·76 | 3·20 |
| 29 H | ............... | 29 | .... | 6·28 | 6·52 | 6·64 | 6·42 .... 6·49 |
| 18 O | ............... | 144 | .... | 31·07 | 35·13 | 32·39 | 31·04 |
| $C^{46}NH^{29}O^{18}$ | .... | 463 | .... | 100·00 | 100·00 | 100·00 | 100·00 |

The analyses are given in mean numbers. Pelletier & Couerbe, who do not state whether they dried their narceine, may have analysed the hydrated alkaloid (Kr.). A specimen of narceine from Robiquet, Pelletier, and Caventou's factory, analysed by Anderson, contained 62·70 p. c. C., 4·22 N., and 6·53 H., corresponding to the formula $C^{32}NH^{19}O^{10}$.

*Decompositions.* 1. Narceine, when cautiously *heated* melts to a yellow, opaque, oily liquid, which at higher temperatures evolves an odour of herrings, turns brown, burns with bright-red smoky flame, and leaves a combustible charcoal (Winckler). It turns yellow at 100°, and when submitted to dry distillation, yields a little coloured acid water, a brown tar having an aromatic odour, and white acid needles, which dissolve in water and alcohol and colour ferric salts blue-black; probably gallic acid (Pelletier). — Narceine heated till it becomes brown gives up to water the substance which blackens ferric salts (Hesse).— — 2. Strong *nitric acid* dissolves narceine with yellow colour, and evolves red fumes when heated therewith; the evaporated solution is bitter, and deposits crystals of oxalic acid (Pelletier; Anderson). In this reaction no cotarnine or meconin (the products obtained from narcotine by similar treatment) is obtained (Anderson). Nitric acid of sp. gr. 1·25 does not colour narceine from poppy capsules, but colours that from opium pale yellowish-red, both varieties dissolving immediately to a clear greenish-yellow liquid (Winckler). Potash liberates from the solution in nitric acid a volatile base (Anderson). — 3. *Oil of vitriol* colours narceine dark red-brown (Winckler); it forms a dark-red solution, which turns green when warmed (Anderson). Hesse's narceine is coloured black, or in thin layers, violet, by oil of vitriol. — Oil of vitriol containing nitric acid, immediately colours narceine brown-red, or with traces of nitric acid, chocolate (Couerbe). A solution in

oil of vitriol is coloured reddish-yellow by permanganate of potash (Guy, *Anal. Zeitschr.* 1, 93).

*Combinations.* — *With Water.* — *Hydrated Narceine?* See above. — Narceine dissolves in 1,285 parts of water at 13° (Hesse); in 375 parts at 14°, and in 230 parts of boiling water (Pelletier), without previously melting to an oil (Winckler). It dissolves easily in boiling water, the solution solidifying to a pulpy mass of silky needles on cooling (Anderson).

Narceine is more easily soluble in *ammonia, potash,* and *soda* than in water; a large quantity of strong potash-ley precipitates it from the solution in the form of an oil, which afterwards solidifies (Anderson). Solution of caustic potash of sp. gr. 1·23 colours aqueous narceine rose-red, and after 24 hours red-brown (Winckler).

*Iodine* colours narceine greyish-blue and brown-violet (Winckler). The black-blue compound of narceine with iodine dissolves without colour in water when boiled therewith, evolving iodine; on cooling, the solution deposits a blue compound containing iodine, a rose-red compound containing only a little iodine, or white narceine free from iodine, according to the length of time it has been boiled (Pelletier).

Narceine dissolves in *acids,* forming crystallisable salts (Pelletier; Anderson). It forms colourless solutions with vegetable acids, or with weak mineral acids; also with strong hydrochloric acid, when the alkaloid is pure (Winckler; Anderson). Pelletier's narceine immediately assumes an azure-blue colour with fuming hydrochloric acid diluted with one-third of water; in a sufficient quantity of water the blue compound forms a colourless solution, acquiring only a transient violet-red colour. On evaporating the colourless solution, there remains a violet-red crust ultimately turning blue, if the narceine has not been decomposed by too large a quantity of hydrochloric acid. If the colourless solution be dehydrated by dropping chloride of calcium into it, the compound is coloured rose-red, violet, and blue; other dehydrating substances produce a similar effect; a certain quantity of water, however, is necessary, since narceine assumes with dry hydrochloric acid gas an orange colour, turning blue only on addition of a little water. From the blue solutions which have been decolorised by the addition of more water, alkalis throw down unchanged narceine. Oil of vitriol diluted with 4 or 5 parts of water, nitric acid diluted with 2 parts of water, and hydrofluosilicic acid act in the same way as hydrochloric acid (Pelletier). Winckler's narceine from poppy-capsules did not exhibit the blue colour; narceine from opium showed it, though only faintly, after being twice recrystallised from alcohol, with the help of animal charcoal. — A saturated aqueous solution of narceine is not affected by oil of vitriol, iodic acid, nitric acid, oxalic acid, or basic acetate of lead; iodide of potassium, tartar-emetic, and nitrate of silver throw down the narceine in needles after 24 hours (Winckler). Sesquichloride of iron does not colour narceine blue (Pelletier), but when added to an aqueous solution it produces in 24 hours a crystalline deposit of hydrochlorate of narceine (Winckler).

*Sulphate of Narceine.* — Crystallises in small prisms from the easily formed solution of narceine in hot dilute sulphuric acid on cooling (Hesse). Silky tufts of needles, resembling narceine (Anderson). The solid salt reddens litmus after prolonged contact with water, but not at

first; boiling water also partially resolves it into narceine and sulphuric acid (Hesse).

*Hydrochlorate of Narceine.* — Separates from a solution of narceine in hydrochloric acid of sp. gr. 1·13, on cooling, in white, semi-lustrous translucent, rhombohedral prisms. The crystals do not redden litmus after the removal of the free acid, but have a distinctly acid, afterwards slightly bitter and styptic taste. They become opaque when gently warmed, and give off their water of crystallisation at 100°. They are nearly insoluble in cold, but freely soluble in hot water, and in 80 p. c. alcohol (Winckler). Anderson obtained short, thick, irregular prisms, having a distinctly acid reaction, and easily soluble in water and alcohol.

|  |  | Dried. |  |  |  | Anderson. |
|---|---|---|---|---|---|---|
| 46 C | .................. | 276 | ........ | 55·25 | ........ | 55·31 |
| N | .................. | 14 | ........ | 2·80 |  |  |
| 30 H | .................. | 30 | ........ | 6·00 | ........ | 6·41 |
| 18 O | .................. | 144 | ........ | 28·85 |  |  |
| Cl | .................. | 35·5 | ........ | 7·10 | ........ | 7·04 |
| C⁴⁶NH²⁹O¹⁸,HCl........ | | 499·5 | ........ | 100·00 |  |  |

|  |  | Crystallised. |  |  |  | Winckler. |
|---|---|---|---|---|---|---|
| C⁴⁶NH²⁹O¹⁸ | .................. | 463 | ........ | 85·03 | ........ | 85·75 |
| HCl | .................. | 36·5 | ........ | 6·70 | ........ | 5·92 |
| 5 HO | .................. | 45 | ........ | 8·27 | ........ | 8·33 |
| C⁴⁶NH²⁹O¹⁸,HCl + 5aq. ........ | | 544·5 | ........ | 100·00 | ........ | 100·00 |

*Nitrate of Narceine.* — Obtained from the hydrochlorate and nitrate of silver. White, dull, silky, delicate prisms, to be freed from adhering silver-salt by washing with cold water. Dissolves less freely than narceine in water (Winckler). From a solution in hot water the salt crystallises in stars (Anderson).

*Chloromercurate of Narceine.* —Mercuric chloride renders hydrochlorate of narceine milky, and when more concentrated, or when left to itself, throws down oily drops, which afterwards crystallise. — White, concentrically arranged, short prisms, which dissolve slightly in boiling water and in hydrochloric acid, and are not coloured by oil of vitriol.

*Chloroaurate of Narceine.* — Yellow precipitate, which dissolves in boiling water, and is deposited in the form of an oil on cooling. It is decomposed by long boiling, with separation of gold (Hesse).

*Chlorplatinate of Narceine.* — Obtained in the form of a crystalline powder or small prisms, or from stronger solutions as an amorphous precipitate, which afterwards crystallises (Hesse; Anderson). Loses 2·73 p. c. of water at 110° (2 at. = 2·61 p. c. HO) (Hesse).

|  |  | at 100°. |  |  |  | Anderson. mean. |  | Hesse. mean. |
|---|---|---|---|---|---|---|---|---|
| 46 C | .................. | 276 | ........ | 41·24 | ........ | 41·05 |  |  |
| N | .................. | 14 | ........ | 2·09 |  |  |  |  |
| 30 H | .................. | 30 | ........ | 4·48 | ........ | 4·60 |  |  |
| 16 O | .................. | 144 | ........ | 21·51 |  |  |  |  |
| 3 Cl | .................. | 106·5 | ........ | 15·94 |  |  |  |  |
| Pt | .................. | 98·7 | ........ | 14·74 | ........ | 14·58 | ........ | 14·52 |
| C⁴⁶NH²⁹O¹⁸,HCl + PtCl² .... | | 669·2 | ........ | 100·00 |  |  |  |  |

Narceine dissolves in 800 parts of dilute *acetic acid* at 13°, and more freely at higher temperatures, crystallising on cooling (Hesse). — *Picric acid* throws down from aqueous narceine a yellow oil soluble in boiling water (Hesse). *Tannic acid* precipitates aqueous narceine (Winckler): *picrotoxin* increases its solubility in water (Pelletier & Caventou, *Ann. Chim. Phys.* 54, 186).

Narceine dissolves in 945 parts of 80 p. c. *alcohol* at 13° (Hesse), and easily in boiling alcohol, but not in *ether*.

*Appendix to Compounds containing 46 atoms of Carbon.*

# 1. Colchicine.

$$C^{34}NH^{19}O^{10}.$$
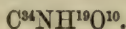
GEIGER & HESSE. *Ann. Pharm.* 7, 274; *Geiger's Handbuch*, 4 ed. 1, 1011.

A. ASCHHOFF; G. BLEY. *N. Br. Arch.* 89, 1; *Pharm. Viertelj.* 6, 377.

L. OBERLIN. *Compt. rend.* 43, 1199; *N. J. Pharm.* 31, 248; *J. pr. Chem.* 71, 112; *N. Br. Arch.* 96, 192; *N. Repert.* 6, 301; *Pharm. Viertelj.* 6, 555; Complete: *N. Ann. Chim. Phys.* 50, 108; *Kopp's Jahresber.* 1856, 548.

WALZ. *N. Jahrb. Pharm.* 16, 1.

LUDWIG & PFEIFFER. *N. Br. Arch.* 111, 3; *Kopp's Jahresber.* 1862, 383.

M. HÜBLER. *N. Br. Arch.* 121, 193; *Chem. Centr.* 1865, 536.

Mistaken for veratrine by Pelletier & Caventou; discovered by Geiger & Hesse in 1833; investigated most fully by Hübler. According to more recent investigations it is not an alkaloïd, but an indifferent nitrogenous vegetable substance.

*Source.* In all parts [even in the flowers (Reithner, *Pharm. Viertelj.* 4, 481)] of *Colchicum autumnale*, and probably in other species of colchicum (Geiger & Hesse). — According to J. Müller (*N. Br. Arch.* 81, 298) *Sem. Colchici* contains colchicine and a base which is coloured purple-red by oil of vitriol [apparently colchiceine (Kr.)].

*Preparation.* 1. *From the seeds,* which need not be bruised (Hübler). The seeds are exhausted with hot alcohol of 90 p. c.; the tinctures are evaporated to a syrup and again diluted with 20 volumes of hot water and left to cool, whereupon a fatty oil is deposited. After separating the deposit, the liquid is precipitated with basic acetate of lead; the precipitate is removed, and also the excess of lead by means of phosphate of soda, and the colchicine is thrown down by previously purified tannic acid, the first and last (less pure) portions of the precipitate being collected separately, and further treated apart from the middle portion. The precipitate is washed (by pressing, suspending in water, collecting, draining, &c.), triturated with oxide of lead and dried; and if an alcoholic solution of a small portion, tested with sesquichloride of iron, is found to be free from tannic acid, the whole is boiled with alcohol. The alcoholic liquid is distilled, and the residual colchicine is dried over the water-bath and afterwards in a vacuum over oil of

vitriol, and is then to be purified by repeated fractional precipitation with tannic acid (Hübler). The liquids precipitated by tannic acid still contain colchicine, which may be recovered by precipitating the excess of tannic acid with basic acetate of lead, and the excess of lead by hydrosulphuric acid, then agitating the filtrate with animal charcoal, which takes up the colchicine and gives it up to boiling alcohol. — The tannic acid employed for the precipitations, if it contains brown colouring matter, as is the case with the commercial acid, must be purified as follows :—A filtered aqueous solution of the acid is evaporated to dryness with oxide of lead ; and the tannate of lead thus formed is boiled repeatedly with alcohol and water in succession, afterwards suspended in water and decomposed by hydrosulphuric acid (Hübler). — Ludwig and Pfeiffer adopt a process similar to Hübler's.

2. The bruised seeds are exhausted with warm alcohol containing sulphuric acid ; the tincture is shaken up with lime ; the filtrate is neutralised with sulphuric acid and freed from alcohol by distillation ; the residual concentrated aqueous liquid is precipitated by carbonate of potash ; the precipitate is pressed, dried, and exhausted with absolute alcohol ; the tincture is decolorised with animal charcoal and evaporated ; and the product is purified by dissolving it in alcohol, with the help of animal charcoal. Or the product is dissolved in dilute sulphuric acid ; the solution is decomposed by excess of quick-lime ; and the colchicine is extracted by ether, dissolved in alcohol and allowed to crystallise, with the addition of a little water (Geiger & Hesse). Are the crystals colchicine or colchiceine? (Kr.).

A. Aschhoff exhausts the roots with cold water ; precipitates the infusion with basic acetate of lead ; neutralises with carbonate of soda not in excess ; precipitates with tannic acid ; washes and presses the precipitate, and dissolves it in 8 parts of alcohol ; digests the solution with freshly precipitated sesquioxide of iron ; and after complete decomposition, evaporates the filtrate and purifies the residue by solution in ether-alcohol.

*Properties.* Amorphous, brittle, fissured mass, which cakes together when triturated. Smells slightly aromatic, like hay, and tastes powerfully and persistently bitter [not acrid (Bley)]. Poisonous ; 0·05 gramme killed a dog, but 0·10 gramme did not kill a rabbit, so that it is probably poisonous only to carnivora (Seidel). See also Schroff (*N. Repert.* 5, 437 ; *Kopp's Jahresber.* 1856, 550) ; Casper (*N. Br. Arch.* 81, 1 ; *Pharm. Centr.* 1855, 139). — Neutral. Softens at 130°, and melts without loss of weight at 140° to a transparent brown mass, which is glassy and brittle after cooling (Hübler). A. Aschhoff, G. Bley, and Ludwig & Pfeiffer also obtained colchicine as an amorphous neutral mass, but that of Walz and of Geiger & Hesse crystallised from weak spirit in colourless needles and prisms, and remained in the form of a varnish on evaporating its solution in stronger alcohol or ether. Inodorous ; does not provoke sneezing, like veratrine ; tastes very bitter and afterwards persistently acrid, not burning ; produces vomiting and purging ; $\frac{1}{12}$th of a grain kills a young cat in twelve hours. Has a slightly alkaline reaction (Geiger & Hesse). Geiger & Hesse's crystals cannot be regarded as colchiceine, the foregoing statements not according sufficiently with the properties of that body (Kr.).

| | at 104°. | | | | Hübler. mean (4). |
|---|---|---|---|---|---|
| 34 C | 204 | ........ | 64·35 | ........ | 64·50 |
| N | 14 | ........ | 4·42 | ........ | 4·45 |
| 19 H | 19 | ........ | 5·99 | ........ | 6·10 |
| 10 O | 80 | ........ | 25·24 | ........ | 24·95 |
| C$^{34}$NH$^{19}$O$^{10}$ | 317 | ........ | 100·00 | ........ | 100·00 |

The substance lost 4 to 6 p. c. of hygroscopic water on drying (Hübler).

*Decompositions.* 1. Colchicine *burns* with a smoky flame on platinum-foil, puffing up and leaving a bulky charcoal (Hübler). — 2. *Chlorine-water* produces in aqueous colchicine a slight yellow precipitate, soluble in ammonia with orange-yellow colour (Aschhoff). — 3. Colchicine is converted into colchiceine by dilute *sulphuric* or *hydrochloric acid* (Oberlin; Hübler). See below.

4. Strong *nitric acid* colours colchicine dark-violet or blue, changing to olive-green and yellow (Geiger & Hesse). Nitric acid free from nitrous acid colours it yellow, brown-red, to violet, afterwards brown-green, and lastly brown-red; fuming nitric acid colours it dark-violet to indigo-blue, afterwards turning yellow (Aschhoff). — 5. *Oil of vitriol*, cautiously poured upon colchicine, assumes a dark-green colour, changing rapidly to yellow as the colchicine dissolves; a glass rod moistened with nitric acid and introduced into the yellow liquid produces a dark-blue zone, changing to violet, brown, and yellow. When supersaturated with ammonia, the solution assumes a dark brick-red colour, which is turned yellow by acids, restored by alkalis, and remains fixed (Hübler). Geiger & Hesse's colchicine is coloured yellowish-brown by oil of vitriol. A solution of colchicine in nitric acid is coloured by oil of vitriol blue-violet, afterwards brownish-yellow, and ultimately yellow. Chromate of potash colours the solution in sulphuric acid green (Aschhoff).

6. Colchicine treated with hot *potash-ley*, yields a brown resin (Aschhoff). — When heated to 100° for a day in a sealed tube with *baryta-water*, it is converted into colchiceïne-baryta (Hübler). — 7. The precipitate produced by *sulphate of copper* in solutions of colchicine dissolves in caustic potash, forming a solution which turns greenish-yellow on boiling, without depositing cuprous oxide (Ludwig & Pfeiffer).

*Combinations.* Colchicine deliquesces slowly in *water* and dissolves in all proportions (Hübler). Geiger & Hesse's colchicine dissolves with moderate facility in water. *Tincture of iodine* thickens aqueous colchicine with carmine-red colour. Aqueous *mineral acids*, especially hydrochloric acid, added to aqueous colchicine, colour it a deep yellow, and decompose it on long standing, but do not combine with it (Hübler; Aschhoff). Geiger & Hesse's colchicine neutralises acids completely, forming salts which are permanent in the air, partially crystallisable, have a very bitter and harsh taste, and dissolve easily in water and alcohol. The base is precipitated by alkalis from concentrated, but not from dilute solutions.

Aqueous *alkalis* colour solutions of colchicine a deep yellow (Hübler). An aqueous solution of colchicine is precipitated by carbonate of potash (Hübschmann, *N. Br. Arch*. 95, 332). An equal volume (not a few drops) of potash-ley produces a yellowish-white precipitate (Aschhoff). Aschhoff & Bley believe they have obtained compounds of colchicine with baryta, lime, and magnesia.

Aqueous colchicine is not precipitated by *neutral or basic acetate of lead, sulphate of copper* (contrary to the statement of Ludwig & Pfeiffer), or *sesquichloride of iron* (Hübler). It yields an orange-yellow precipitate with *phosphomolybdic acid* (Sonnenschein). *Mercuric chloride* throws down from its concentrated aqueous solution a white curdy precipitate, soluble in excess of the precipitant and in alcohol (Ludwig & Pfeiffer;

Hübler). *Terchloride of gold* produces a whitish-yellow precipitate, soluble in water, alcohol, and excess of the precipitant. *Bichloride of platinum* does not precipitate aqueous colchicine (Hübler; Bley), or throws down from concentrated solutions only a precipitate soluble in alcohol and in bichloride of platinum (Ludwig & Pfeiffer). According to Geiger & Hesse, chloride of platinum throws down a yellow precipitate from aqueous colchicine, but not from its salts. See also Walz on the reactions of aqueous colchicine (*loc. cit.*).

*Tannate of Colchicine.* — Aqueous tannic acid throws down curdy flocks from an aqueous solution of colchicine, even when very dilute. — White amorphous powder, fusible without decomposition above 140°. Hygroscopic; inodorous; less bitter than colchicine. — Dissolves slightly in cold, more freely in boiling water, and to a less extent in saline solutions. Easily soluble in alcohol; insoluble in ether (Hübler). Dissolves in aqueous carbonate of potash, and in acetic acid (Aschhoff).

|  |  | at 104°. |  |  |  | Hübler. |
|---|---|---|---|---|---|---|
| 210 C | .................................... | 1260 | ........ | 57·61 | ...... | 57·9 to 58·3 |
| 3 N | .................................... | 42 | ........ | 1·92 | ........ | 1·98 |
| 101 H | .................................... | 101 | ........ | 4·62 | ........ | 4·8 to 4·9 |
| 98 O | .................................... | 784 | ........ | 35·85 |  |  |
| 3 C³⁴NH¹⁹O¹⁰,2C⁵⁴H²²O³⁴ | .... | 2187 | ........ | 100·00 |  |  |

Hübler supposes the compound to contain 2HO less.

Colchicine dissolves easily in *alcohol;* according to Hübler, it is insoluble, according to Geiger and Hesse soluble in *ether.* Hübschmann (*N. Jahrb. Pharm.* 16, 1) found it soluble in 18 parts of ether of sp. gr. 0·74, and less soluble in absolute ether.


## 2. Colchiceïne.

$$C^{34}NH^{19}O^{10} = C^{34}NH^{19}O^6,H^4.$$
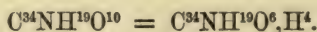
OBERLIN. *N. Ann. Chim. Phys.* 50, 108.
LUDWIG & PFEIFFER. *N. Br. Arch.* 111, 3.
HÜBLER. *N. Br. Arch.* 121, 193.

Discovered by Oberlin; more fully investigated by Hübler. — Occurs, according to Oberlin, in *Colchicum autumnale,* but his own experiments show that the colchicine contained therein undergoes conversion into colchiceïne.

*Formation and Preparation.* When an aqueous solution of colchicine, prepared by Geiger and Hesse's process, is mixed with sulphuric acid, it assumes a yellow colour, and after being heated for some time throws down, on addition of water, a yellow precipitate of colchiceïne, which may be crystallised from alcohol or ether. Colchiceïne likewise crystallises from a solution of colchicine mixed with hydrochloric acid, after standing in the cold for some weeks; in this case the product is less coloured and more easily purified than that made with sulphuric acid (Oberlin). — Hübler dissolves 5 parts of colchicine in 100 parts of water, and mixes the solution with 5 parts of oil of vitriol previously diluted with water. The liquid assumes a yellow colour, evolves a penetrating odour, and when heated turns cloudy from separation of

resinous drops, after the removal of which, the somewhat concentrated solution solidifies on cooling to a greenish-yellow crystalline mass, which is purified by 8 or 10 times repeated crystallisation from water. A large additional quantity of colchiceïne may be obtained by boiling the resinous drops with water. — Colchicine is also converted into colchiceïne by boiling with baryta-water (p. 603) (Hübler).

The crystals thus obtained are free from the acid employed (Oberlin). Colchiceïne is formed without the simultaneous formation of sugar (Ludwig & Pfeiffer), or of any second product; the resin formed at the same time is to be regarded as a secondary decomposition-product of colchiceïne (Hübler). Walz thought he had discovered the formation of a substance which reduced oxide of copper, and three other bodies.

A part of the resin remains dissolved in the colchiceïne mother-liquor, and may be precipitated in flocks by exactly neutralising the liquid with carbonate of soda; or it may be obtained by evaporating the mother-liquor and exhausting the residue with alcohol. It forms an amorphous, bitter mass, soluble with deep-red colour in acids, alkalis, ether, alcohol, and aqueous ammonia, and with blood-red colour in nitric acid (Hübler; Oberlin).

*Properties.* Small, white needles collected in nodules, or pearly laminæ. According to Oberlin and Ludwig & Pfeiffer, it tastes very bitter; according to Hübler, less bitter than colchicine. Permanent in the air. Softens when heated, and melts at 155° (Oberlin). According to Oberlin neutral, according to Hübler acid, especially in alcoholic solution. Not poisonous to rabbits in doses of half a gramme (Oberlin).

|  | *Calc. according to Hübler.* | | | Hübler. *mean*, at 100°. | | Oberlin. |
|---|---|---|---|---|---|---|
| 34 C | ............... | 204 | ........ | 64·35 | ........ 64·45 ........ | 62·67 |
| N | ............... | 14 | ........ | 4·42 | ........ 4·50 ........ | 4·30 |
| 19 H | ............... | 19 | ........ | 5·99 | ........ 6·10 ........ | 6·56 |
| 10 O | ............... | 80 | ........ | 25·24 | ........ 24·95 ........ | 26·47 |
| $C^{34}NH^{19}O^{10}$ ........ | | 317 | ........ | 100·00 | ........ 100·00 ........ | 100·00 |

Isomeric with colchicine (Hübler).

*Decompositions.* 1. Colchiceïne assumes a yellow colour externally when exposed to diffused *light*; the colourless solution likewise leaves a yellowish-brown stain when dried on paper (Hübler). — 2. It is coloured by *heating* to 200°, melts on platinum-foil, and burns (Oberlin). — 3. *Chlorine-water* throws down white flocks from solutions of colchiceïne (Ludwig & Pfeiffer). — 4. Colchiceïne forms, with *oil of vitriol*, a deep-yellow solution, which, when diluted with water and left to itself, deposits brown flocks (Oberlin). — 5. The deep-yellow solution in strong *nitric acid* rapidly assumes a violet colour, changing to dark-red and light-red, and ultimately to yellow (Oberlin). The aqueous solution is coloured violet, afterwards brown, by nitric acid, yellow by the dilute acid (Ludwig & Pfeiffer).— 6. Colchiceïne, subjected to prolonged boiling with dilute *mineral acids*, yields a resin similar to that formed in its preparation (Hübler).

*Combinations.* Colchiceïne dissolves slightly in cold, and more freely in boiling *water*. Dilute *mineral acids* colour the solution yellow;

*acetic acid* does not affect it (Oberlin). — *Iodine-water* throws down brown flocks from the aqueous solution (Ludwig & Pfeiffer).

Colchiceïne behaves towards *bases* like an acid. It dissolves easily in aqueous *ammonia*, remaining free from ammonia when evaporated. It dissolves in potash- and soda-ley, and in aqueous alkaline carbonates, liberating carbonic acid; the latter solutions, when evaporated, leave the potash- and soda-salts in the form of yellow fissured varnishes (Hübler).

*Baryta-salt.* — Baryta dissolved in wood-spirit throws down from a similar solution of colchiceïne, a jelly which dissolves in wood-spirit and in excess of baryta (Oberlin). The soda-salt throws down from chloride of barium, amorphous white flocks, which dissolve when heated, and re-appear on cooling (Hübler). — Colchiceïne is boiled with baryta-water; the excess of baryta is removed by means of carbonic acid; the solution is evaporated; and the residue is dissolved in alcohol, filtered, and evaporated. — Amorphous yellow mass, soluble in alcohol (Hübler).

|  | at 100°. |  |  | Hübler. |
|---|---|---|---|---|
| $C^{34}NH^{18}O^9$ ............ | 308 | ........ | 80·10 |  |
| BaO ............... | 76·5 | ........ | 19·90 | ........ 18·9 |
| $C^{34}NH^{18}BaO^{10}$ .... | 384·5 | ........ | 100·00 |  |

Colchiceïne-soda throws down from *chloride of calcium* and *chloride of magnesium* white amorphous flocks; it produces with *zinc-, lead-, bismuth-,* and *mercury-salts,* white precipitates, soluble in excess of the salts, or on boiling, re-appearing as the liquid cools. It forms a red-brown precipitate with *nitrate of cobalt;* greenish-brown with *sesquichloride of iron.* All these precipitates are soluble in alcohol (Hübler). — Colchiceïne does not precipitate *neutral or basic acetate of lead, mercuric chloride, nitrate of silver, or tincture of galls.* An alcoholic solution is not precipitated by *bichloride of platinum* (Oberlin). Ludwig & Pfeiffer's colchiceïne forms a fine light-yellow precipitate with *chloride of gold* and *picric acid,* dirty dark-brown with *bichloride of platinum,* and pale-brown with *tannic acid* after addition of hydrochloric acid, but is not precipitated by *mercuric chloride.*

*Colchiceïne with Cupric oxide.* — By decomposing the soda-compound of colchiceïne with sulphate of copper, a yellowish-green precipitate is obtained, which turns darker and crystalline on boiling, and is easily soluble in excess of the copper-salt and in alcohol. — Or alcoholic colchiceïne is boiled with freshly precipitated cupric hydrate, and the green filtrate is diluted with water and the alcohol driven off, whereupon the copper-compound is deposited. — Microscopic, apparently quadratic tables and octohedrons. Dissolves slowly in strong aqueous ammonia and in hot potash-ley (Hübler).

|  |  |  |  | Hübler. |
|---|---|---|---|---|
| $C^{34}NH^{18}O^9$ ............ | 308 | ........ | 88·56 |  |
| CuO ............ | 39·8 | ........ | 11·44 | ........ 9·36 |
| $C^{34}NH^{18}CuO^{10}$ .... | 347·8 | ........ | 100·00 |  |

According to Hübler, the substance contained an admixture of free colchiceïne.

Colchiceïne dissolves in *wood-spirit* and in *alcohol,* from which it crystallises, and less freely in *ether.* It does not crystallise from its easily

formed solution in *chloroform* (Hübler; Oberlin). It is withdrawn from its solutions by *animal charcoal*, which afterwards gives up to alcohol, not colchiceïne, but a brown bitter mass (Ludwig & Pfeiffer; Hübler).

# 3. Corydaline.

WACKENRODER. *Kastn. Arch.* 7, 417; *Berz. Jahresber.* 7, 220. — *Kastn. N. Arch.* 2, 427. — *N. Br. Arch.* 49, 153; *Kopp's Jahresber.* 1847 and 1848, 644.
PESCHIER. *Mém. de la Société de Phys.* 4, 247; *N. Tr.* 17, 2, 80.
WINCKLER. *Pharm. Centr.* 1832, 301; *N. Br. Arch.* 49, 301.
FR. DÖBEREINER. *N. Br. Arch.* 13, 64; *Ann. Pharm.* 28, 288.
RUIKHOLDT. *N. Br. Arch.* 49, 139; *Ann. Pharm.* 64, 369; *Kopp's Jahresber.* 1847 and 1848, 643.
J. MÜLLER. *Pharm. Viertelj.* 8, 536.
C. LEUBE, jun. *Pharm. Viertelj.* 9, 524.

Discovered by Wackenroder in 1826. — Occurs in the roots of *Corydalis tuberosa* and *C. fabacea* (Wackenroder). In smaller quantity in the leaf-sap of the first plant (Peschier).

*Preparation.* 1. The coarsely powdered root is twice digested with water containing hydrochloric acid and pressed; the liquid is left to itself till it clears, and is then precipitated with carbonate of soda; and the precipitate is washed so long as it gives up colouring matter, dissolved in water containing hydrochloric acid, and again thrown down by carbonate of soda. The well-washed, dried, and triturated precipitate is now dissolved by shaking it with freshly rectified oil of turpentine, and the filtered wine-red solution is agitated with water containing hydrochloric acid, and thereby freed from corydaline. The oily layer is decanted; the acid solution is filtered through a wet filter and precipitated with caustic potash; and the precipitate is washed and dried (Müller). — 2. The coarsely powdered root is macerated for a few days with pure water, and afterwards repeatedly with water containing sulphuric acid; the liquids are filtered and precipitated by carbonate of soda; and the precipitates are exhausted with alcohol (those from the last macerations, being less pure, are treated separately). The alcoholic filtrate is evaporated; the residue is dissolved in dilute sulphuric acid; the solution is filtered from green resin, and mixed, first with a little potash, which throws down dark-coloured corydaline, and, after filtration, with more potash, whereby purer corydaline is precipitated (Wackenroder). — Or an alcoholic extract of the root may be exhausted with water; the solution precipitated with basic acetate of lead in not too great excess; the filtrate freed from lead by hydrosulphuric acid; and the corydaline precipitated by potash or lime. — Or the root is boiled with water containing hydrochloric acid; the extract is evaporated to dryness and exhausted with alcohol; the alcoholic solution is evaporated; the residue taken up by water, which leaves resin behind; and the corydaline is precipitated from the solution by caustic potash (Wackenroder).

Winckler frees the sap of the fresh root from albumin by boiling; precipitates the filtrate with basic acetate of lead; separates the precipitate; and afterwards removes the excess of lead by sulphuric

acid, and precipitates with ammonia not in excess.  The precipitate is collected, washed with cold water, dried, and exhausted with hot alcohol of 80 p. c., whereby a dark-green tincture is obtained, which leaves white crystalline corydaline on evaporation.

*Properties.*   White loose powder, appearing under a magnifying-power of 125 diameters, to be made up of amorphous granules (Müller; Leube).   According to Wackenroder, it crystallises, on evaporating its alcoholic solution, in colourless prisms and thin scales.   It softens at 60°, and melts completely at 70° [far below 100° (Wackenroder)] to a translucent wax, without losing weight (Müller).   Melted corydaline floats on water.   It is inodorous, and has but little taste alone, but is very bitter in solution.   Its alcoholic solution has an alkaline reaction (Wackenroder).

|   | | Döbereiner. | | Ruikholdt. at 62°. | | Müller. at 50°. | | Leube. *mean.* |
|---|---|---|---|---|---|---|---|---|
| C | .... | 62·18 | ........ | 59·70 | ........ | 74·11 | ........ | 74·18 |
| N | .... | 4·32 | ........ | 3·02 | ........ | 3·67 | ........ | 3·62 |
| H | .... | 6·84 | ........ | 5·90 | ........ | 7·67 | ........ | 7·54 |
| O | .... | 26·66 | ........ | 31·38 | ........ | 14·55 | ........ | 14·66 |
|   | | 100·00 | ........ | 100·00 | ........ | 100·00 | ........ | 100·00 |

C³⁴NH²²O¹⁰ (Döbereiner) ;  C⁴⁵NH²⁷O¹⁸ (Ruikholdt) ;  C⁹²N²H⁵⁸O¹⁴ (Müller). Leube halves this formula.

*Decompositions.*   1. Precipitated corydaline (and the crystallised substance to a less extent) assumes a greenish-yellow [lemon-yellow (Müller)] colour in *sunlight*, and cannot afterwards be decolorised by animal charcoal (Wackenroder). — 2. When *heated* above its melting-point it turns brown, evolves easily combustible vapours, having an empyreumatic and ammoniacal odour, and burns with a yellow luminous flame. — 3. It dissolves with yellow colour in strong *nitric acid* (Müller) ; according to Wackenroder and Ruikholdt, it colours the acid blood-red [on account of the presence of resin (Müller)] and dissolves without decomposition. — 4. Corydaline forms, with *oil of vitriol*, a dark-red solution (Müller), which, when evaporated, changes to violet and black, and carbonises (Wackenroder).

*Combinations.*   Corydaline does not dissolve in *water* either cold or boiling (Müller). — With *acids* it forms salts, which, according to Müller and Leube, are amorphous, resinous, and easily fusible ; according to Wackenroder, crystallisable for the most part.   Caustic alkalis and their carbonates, as well as ammonia, throw down corydaline from its salts as a white precipitate, insoluble in excess of the precipitant (Müller).   Wackenroder at one time described corydaline as nearly insoluble in alkalis, but afterwards stated that it is easily soluble in excess of potash-ley and precipitable from the solution by sal-ammoniac.

*Sulphate of Corydaline.* — The greenish slightly acid solution leaves on evaporation a crystalline residue, only partially soluble in water. The aqueous solution leaves, when evaporated, a greenish-yellow transparent mass, soluble in water, alcohol, and ether (Wackenroder).

*Hydrochlorate of Corydaline.* — A solution of corydaline in excess of hydrochloric acid leaves, on evaporation, a residue soluble in water, alcohol, and ether (Wackenroder). By digesting excess of corydaline in hydrochloric acid, Wackenroder & Ludwig subsequently obtained an acid yellowish-green liquid which yielded crystals when treated with animal charcoal. The crystals are yellowish-green right rhombic prisms, having a vitreous lustre, very brittle, and neutral; when dissolved in alcohol of 96 p. c. they are again deposited in the form of a greyish-yellow crystalline powder. They give off 12·5 p. c. water at 100°, and 3·02 p. c. more at 145° to 170°, and in the air-dried state contain 10·78 p. c. of hydrochloric acid (Wackenroder & Ludwig).

*Nitrate of Corydaline.* — Sulphate of corydaline and nitrate of baryta yield prismatic crystals, which resinise when too strongly heated (Peschier). Very dilute nitric acid dissolves corydaline without decomposition, but the solution reddens and decomposes when evaporated (Wackenroder).

*Chloromercurate of Corydaline.* — Thrown down from hydrochlorate of corydaline by mercuric chloride as a white precipitate (Müller), containing, at 100°, 12·98 p. c. chlorine, and agreeing with the formula $C^{46}NH^{29}O^{7},HCl,HgCl$ (Leube).

*Chloroplatinate of Corydaline.* — Yellow precipitate containing, at 100°, 16·89 p. c. platinum (Leube).

*Terchloride of gold* throws down a yellow precipitate from hydrochlorate of corydaline (Müller).

*Acetate of Corydaline.* — Strong acetic acid dissolves corydaline slowly, and leaves on evaporation a crystalline compound, soluble in water, alcohol, and ether (Wackenroder).

Hydrochlorate of corydaline is precipitated by *tannic acid* and by *tincture of galls.*

Corydaline dissolves in about 9 parts of cold 90 p. c. *alcohol*, in all proportions in the hot liquid, and in 2½ to 3 parts of *ether* (Müller). It is insoluble in *oils* both *fat* and *volatile* (Wackenroder).

# ADDENDA.

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## Cinchonine.

O. HESSE. *Ann. Pharm.* cxxxv, 338; *Bull. Soc. Chim.* 1866, i, 462.

*Bihydriodate of Cinchonine*, $C^{40}N^2H^{24}O^2,HI + 2HO$, crystallises in golden-yellow laminæ, gives off its water at 100°, re-absorbs it again in damp air. Gives by analysis 3·17 p. c. water and 44·31 iodine (calc. 3·09 HO, and 43·64 I.).

*Chloroaurate of Cinchonine*, $C^{40}N^2H^{24}O^2,2HCl,AuCl^3$. Heavy yellow powder, melting to a dark-yellow mass at a few degrees above 100°, and yielding 39·51 p. c. gold (calc. 39·87 p. c.).

*Tartrate of Cinchonine and Antimony.* — This salt contains 2·47 p. c. water of crystallisation, not 24·77, as stated at page 218; and it is *not* efflorescent.

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## Cinchonidine.

HESSE. *Ann. Pharm.* cxxxv, 333; *Bull. Soc. Chim.* 1866, i, 460.

This base, the quinidine of Winckler,* is contained in small quantity in all Calisaya barks, and is consequently obtained, together with quinine, in the preparation of the latter on the large scale. As the complete separation of quinine from cinchonidine is difficult, commercial cinchonidine almost always contains small quantities of quinine. According to Koch (*Arch. Pharm.* cxlii, 34), cinchonidine possesses febrifugal properties.

*Purification.* Commercial cinchonidine containing quinine is precipitated with solution of Rochelle salt, the precipitate is dissolved in hydrochloric acid, and the solution precipitated with excess of am-

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* Hesse retains the name quinidine for this base, and designates the quinidine of Pasteur (p. 221) as *conchinine*; but as the base discovered by Winckler is someric, not with quinine, but with cinchonine, it is more appropriately named *icinchonidine*.

monia. The alkaloïds thus obtained are separated as far as possible by treatment with ether, the quinine being thereby dissolved, together with a not inconsiderable portion of the cinchonidine; the undissolved portion, consisting chiefly of cinchonidine, is dissolved in hydrochloric acid; and the neutral hydrochlorate of cinchonidine thus obtained is purified by recrystallisation from water.

*Properties.* Cinchonidine crystallises from alcohol in large anhydrous prisms, melting at 206·5° (corrected) to a colourless mass, which solidifies in the crystalline form at about 190°.

|  |  |  |  |  | Hesse. mean. |
|---|---|---|---|---|---|
| 40 C | ............. | 240 | ........ | 77·92 | ........ 77·71 |
| 2 N | ............. | 28 | ........ | 9·09 | |
| 24 H | ............. | 24 | ........ | 7·79 | ........ 7·80 |
| 2 O | ............. | 16 | ........ | 5·20 | |
| $C^{40}N^2H^{24}O^2$ | .... | 308 | ........ | 100·00 | |

This formula had not previously been established by direct analysis (see page 222).

Cinchonidine dissolves in 1680 pts. of water at 10°, somewhat more freely in boiling water.

The salts of cinchonidine are easily prepared either by saturating the alcoholic solution of the base with an acid, or, in the case of salts much less soluble than the hydrochlorate, by double decomposition between that salt and the soda-salt of the required acid.

*Hypophosphite of Cinchonidine* crystallises in delicate white prisms much more soluble than those of the corresponding quinine-salt; it may be recrystallised from boiling water.

*Hyposulphite of Cinchonidine,* $2C^{40}N^2H^{24}O^2,S^4H^2O^6 + 4HO.$ — Thin white prisms, which easily give off their water of crystallisation amounting to 4·56 — 4·83 p. c. (4 at. = 4·70 p. c.) at 110°, but recover it all on exposure for a short time to moist air. 1 pt. of the salt dissolves in 221 pts. water at 10°.

*Sulphate of Cinchonidine* (comp. p. 224). — a. *Mono-acid,* $2C^{40}N^2H^{24}O^2$, $S^2H^2O^8 + 12HO.$ Crystallises in white prisms, which give off all their water, except ½ p. c., on exposure to the air, and the rest (12·92—13·14 p. c. in all) at 100°. One part of the salt dissolves in 97·5 pts. water at 12°. It is insoluble in ether.

|  | *Anhydrous.* |  |  |  | Hesse. |
|---|---|---|---|---|---|
| 2 $C^{40}N^2H^{24}O^2$ | ............. | 616 | ........ | 86·28 | |
| $S^2H^2O^8$ | ............. | 98 | ........ | 13·72 | ........ 13·56—13·93 |
| $2C^{40}N^2H^{24}O^2,S^2H^2O^2$ | ........ | 714 | ........ | 100·00 | |

|  | *Hydrated.* |  |  |  | Hesse. |
|---|---|---|---|---|---|
| 2 $C^{40}N^2H^{24}O^2$ | ............. | 616 | ........ | 74·95 | |
| $S^2H^2O^8$ | ............. | 98 | ........ | 11·92 | ........ 11·96 |
| 12 HO | ............. | 108 | ........ | 13·13 | ........ 12·92—13·14 |
| $2C^{40}N^2H^{24}O^2,S^2H^2O^8 + 12aq.$ | .... | 822 | ........ | 100·00 | |

Hesse describes also a modification of the anhydrous salt which is produced "under circumstances not exactly known," and crystallises, from boiling water, in beautiful colourless prisms, or, when its aqueous solution is left to evaporate at a moderate temperature, in warty masses containing only traces of water. This anhydrous salt dissolves, according to Hesse, in the same quantity of water as the hydrated salt, and appears to contain a peculiar alkaloïd, inasmuch as when the alkaloïd separated from it, is dissolved in hydrochloric acid, a hydrochlorate is obtained, which when decomposed by sulphate of soda, yields the original anhydrous sulphate, and when treated with oxalate of ammonia, yields an anhydrous oxalate of cinchonidine (p. 613). But if, on the other hand, the hydrochloric solution of the anhydrous cinchonidine be mixed with sodio-potassic tartrate, and the resulting tartrate of cinchonidine converted into a sulphate, the sulphate thus produced is identical in every respect with the hydrated salt a.

b. *Bi-acid.* — A solution of 1 at. of the monosulphate (a) in 1 at. sulphuric acid, evaporated down to a small bulk, yields this salt in long, colourless, striated prisms, very efflorescent, and easily soluble in water and in alcohol. The aqueous solution has a strong acid reaction, and exhibits a blue fluorescence by reflected light. The crystals give off their water at 120°.

|  |  | *Crystals.* |  |  | Hesse. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | .............................. | 308 | ........ | 62·09 |  |
| $S^2H^2O^8$ | .............................. | 98 | ........ | 19·76 | ........ 20·26 |
| 10 HO | .............................. | 90 | ........ | 18·15 | ........ 18·25 |
| $C^{40}N^2H^{24}O^2,S^2H^2O^3$ + 10aq. | .... | 496 | ........ | 100·00 |  |

This analysis agrees very nearly with that of Winckler (p. 224).

c. *Quadri-acid.* — The solution of the bisulphate in dilute sulphuric acid, evaporated over oil of vitriol at ordinary temperatures, ultimately yields short, solid, colourless prisms of the quadrisulphate, which dissolve but slowly in cold water, so that they may be easily freed from excess of acid by washing with cold water. The salt is insoluble in ether, which, moreover, does not take from it any portion of the acid. The aqueous solution is strongly acid, and exhibits an intense blue fluorescence by reflected light.

|  |  |  |  |  | Hesse. |
|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | ......................... | 308 | ........ | 57·04 |  |
| 2 $S^2H^2O^8$ | ......................... | 196 | ........ | 36·29 | ........ 36·16 |
| 4 HO | ......................... | 36 | ........ | 6·67 | ........ 7·11 |
| $C^{40}N^2H^{24}O^2,2S^2H^2O^9$ + 4aq. | .... | 540 | ........ | 100·00 |  |

*Bihydriodate of Cinchonidine,* $C^{40}N^2H^{24}O^2,2HI$ + $2HO$. On adding a dilute solution of the hydrochlorate to a solution of potassium-iodide heated to about 50°, the liquid becomes milky, and ultimately deposits the bi-hydriodate in fine lemon-yellow prisms, which, at 120°, give off 3·17 to 3·22 p. c. water (4HO = 3·09 p. c.).

*Hydrochlorate of Cinchonidine,* $C^{40}N^2H^{24}O^2,HCl$ + $2HO$. Crystallises by evaporation in large monoclinic double pyramids, which dissolve in 38·5 pts. water at 10°, in 20 pts. water at 20·1°, and in 325 pts. ether at 10° (comp. p. 225). The crystals give off 4·87 to 5·11 p. c. water at 120° (calc. for 2HO. = 4·96 p. c.), and yield by analysis 9·85 to 9·94 p. c. chlorine (calc. 9·79 p. c.).

If the solution is concentrated at a high temperature, the salt finally separates in yellowish oily drops, which, after cooling, gradually

solidify to a radio-crystalline mass, probably consisting of the anhydrous salt. The same product is obtained, though in small quantity, when the solution is evaporated at a gentle heat.

*Nitrate of Cinchonidine* crystallises in large colourless prisms, which melt at about 100° to an oily mass. When the aqueous solution is too quickly evaporated, the salt likewise separates in the oily form, but if kept under water, solidifies after a while in crystals. 1 pt. of the salt dissolves in 70·5 pts. water at 10°. The crystals give off their water (2 at.) at 110°.

|  | | Crystals. | | | | | | | Hesse |
|---|---|---|---|---|---|---|---|---|---|
| $C^{40}N^2H^{24}O^2$ | | 308 | ........ | 79·17 | ........ | 79·05 | ........ | 78·93 |
| $NHO^6$ | | 63 | ........ | 16·21 | | | | |
| 2 HO | | 18 | ........ | 4·62 | ........ | 4·80 | | |
| $C^{40}N^2H^{24}O^2,NHO^6 + 2aq.$ | .... | 389 | ........ | 100·00 | | | | |

*Chloroaurate of Cinchonidine*, $C^{40}N^2H^{24}O^2,2HCl,AuCl^3$. Obtained by precipitating a dilute aqueous solution of the hydrochlorate with chloride of gold, at ordinary temperatures, as a pulverulent mass of a fine yellow colour, melting with decomposition at about 100°. When dried over oil of vitriol, it contains 40·04 p. c. gold, the formula requiring 39·87 p. c.

*Chloroplatinate of Cinchonidine*, $C^{40}N^2H^{24}O^2,2HCl,2PtCl^2 + 2HO$. A hot acid aqueous solution of the hydrochlorate, mixed with platinic chloride, deposits this salt after a few seconds as a pale orange-yellow crystalline powder, or more rarely in small flattened prisms. It is nearly insoluble in cold, slightly soluble in boiling water, and gives off its water of crystallisation, 2·07 to 2·42 p. c. (2 at. = 2·43 p. c.), between 120° and 130°. The hydrated salt gives by analysis 26·83 platinum (calc. 26·73 p. c.); the salt dried at 130° gives 27·32 to 27·44 p. c. platinum (calc. 27·40 p. c.).

*Hydroferrocyanate of Cinchonidine.* — Obtained by adding ferrocyanide of potassium to the solution of any cinchonidine-salt in dilute sulphuric acid, as an egg-yellow precipitate consisting of spherical aggregations. Moderately dilute solutions sometimes yield laminæ, exactly resembling the corresponding cinchonine-salt. Hence the reaction given by Bills (p. 214) for the detection of cinchonine may also be applied to the detection of cinchonidine.

*Acetate of Cinchonidine*, $C^{40}H^{24}N^2O^2,C^4H^4O^4 + 2HO$. — Obtained by saturating an alcoholic solution of cinchonidine with acetic acid, evaporating, and dissolving the separated salt in a small quantity of water, in nodular groups of small white needles very soluble in water, whether cold or hot. It gives off its water of crystallisation, together with a considerable proportion of its acid, at 100°, so that it is afterwards only partially soluble in cold water. The air-dried salt gives by analyis 79·39 p. c. cinchonidine (calc. 79·79 p. c.).

*Neutral Oxalate of Cinchonidine.* — a. *Anhydrous.* $2C^{40}N^2H^{24}O^2,C^4H^2O^8$. — Obtained by adding oxalate of ammonia to the hydrochloric acid solution of the base precipitated from the anhydrous sulphate (p. 612). Forms small white nodules consisting of concentrically grouped prisms, which do not lose weight at 110°. Contains 10·18 p. c. oxalic acid, $C^4H^2O^8$ (calc. 10·19 p. c.).

b. *Hydrated,* $2C^{40}N^2H^{24}O^2,C^4H^2O^8 + 12HO.$ — Obtained by precipitation from the ordinary hydrochlorate. Crystallises in long asbestiform prisms, which, when in mass, shrink together to an extraordinary degree on drying in the air. 1 pt. of the hydrated salt dissolves in 252 pts. water at 10°. The air-dried salt gives off 12·72 to 12·87 p. c. water at 110° (calc. for 12HO = 13·26). The difference arises from loss of a small quantity of water at ordinary temperatures.

*Succinate of Cinchonidine,* obtained by saturating an alcoholic solution of cinchonidine with succinic acid, forms small white prisms, which retain their water of crystallisation when dried over oil of vitriol, but give it off at 100°, and dissolve in 582·5 pts. water at 10°.

|  |  | Crystals. |  |  |  | Hesse. |
|---|---|---|---|---|---|---|
| $2C^{40}N^2H^{24}O^2$ | | 616 | .... | 80·00 | .... | 79·49 |
| $C^8H^6O^8$ | | 118 | .... | 15·33 | | |
| 4 HO | | 36 | .... | 4·67 | .... | 4·78—4·85 |
| $2C^{40}N^2H^{24}O^2,C^8H^6O^8 + 4aq.$ | .... | 770 | .... | 100·00 | | |

*Tartrate of Cinchonidine (neutral).* — Obtained by double decomposition from somewhat concentrated solutions, as a white crystalline precipitate, quite insoluble in sodio-potassic tartrate. Boiling water dissolves it sparingly, and deposits it on cooling in fine white prisms. 1 pt. of the salt requires for solution 12·65 parts of water at 10°. Neutral tartrate of cinchonine requires only 35·6 pts. at 16° to dissolve it (the hydrated salt 33 pts.), so that cinchonine and cinchonidine may easily be separated by the different solubilities of their tartrates. The crystals give off their water completely between 100° and 120°, but recover it all on exposure to moist air.

|  |  | Crystallised. |  |  |  | Hesse. |
|---|---|---|---|---|---|---|
| 88 C | | 528 | ........ | 65·83 | ........ | 66·05 |
| 4 N | | 56 | ........ | 6·98 | | |
| 58 H | | 58 | ........ | 7·22 | ........ | 7·33 |
| 20 O | | 160 | ........ | 19·97 | | |
| $2C^{40}N^2H^{24}O^2,C^8H^6O^8 + 4aq.$ | .... | 802 | ........ | 100·00 | | |

Or :

|  |  | | | | Hesse. |
|---|---|---|---|---|---|
| $2C^{40}N^2H^{24}O^2,C^8H^6O^8$ | ................ | 766 | .... | 95·52 | |
| 4 HO | | 36 | .... | 4·48 | .... 4·45 to 4·93 |
| $2C^{40}N^2H^{24}O^2,C^8H^6O^8 + 4aq.$ | .... | 802 | .... | 100·00 | |

*Tartrate of Antimony and Cinchonidine,* obtained like the corresponding cinchonine-salt (p. 218), crystallises in fine white prisms moderately soluble in boiling water, and crystallising in solid prisms on cooling. Very soluble in alcohol.

*Citrate of Cinchonidine.* — A solution of 1 at. acetate of cinchonidine and 2 at. citric acid in a small quantity of water, deposits at a certain degree of concentration colourless prisms, which probably consist of monobasic citrate of cinchonidine, but decompose when dissolved in hot water, the solution yielding a salt containing 2 at. cinchonidine to 1 at. citric acid. This bibasic salt is likewise obtained by decomposing hydrochlorate of cinchonidine with citrate of soda. It gives off 15·39 p. c. water at 120°, and contains 68·31 p. c. cinchonidine.

*Benzoate of Cinchonidine*, $C^{40}N^2H^{24}O^2,C^{14}H^6O^4$, crystallises in short white anhydrous prisms, which dissolve in 340 pts. of water at 10°. — Gives by analysis 71·82 p. c. cinchonidine (calc. 71·62 p. c.).

Cinchonidine dissolves in 19·7 pts. *alcohol* at 80 p. c. at 10°, and in 15·3 pts. at 20°; in 76·4 pts. ether at 10°.

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## Quinine.

O. Hesse. *Ann. Pharm.* cxxxv, 325 ; *Bull. Soc. Chim.* 1866, i, 459.

*Crystallised Quinine*, $C^{40}N^2H^{24}O^4 + 6HO$. — Ordinary amorphous quinine, precipitated from the hydrochlorate by ammonia, gradually absorbs water if left in the liquid, especially in presence of free ammonia, and assumes a crystalline aspect. If a considerable excess of ammonia is present, isolated crystals are formed, which, when magnified, exhibit the form of square prisms with pyramidal summits. The hydrate gives off all its water when left over oil of vitriol. It melts at 57°, whereas anhydrous quinine melts only at 176·8°.

*Phosphate of Quinine* (comp. p. 226). — Obtained by decomposing the hydrochlorate with phosphate of soda. When crystallised from boiling water, it forms tufts of long needles, soluble in 784 pts. water at 10°.

|  |  | *Crystals.* |  |  | Hesse. |
|---|---|---|---|---|---|
| 2 $C^{40}N^2H^{24}O^4$ | 648 | ........ | 72·82 |  |  |
| $PO^5$ | 71 | ........ | 7·98 | ........ | 8·11 |
| 3 HO | 27 | ........ | 3·03 |  |  |
| 16 HO | 144 | ........ | 16·17 | ........ | 16·05 to 16·52 |
| $C^{40}N^2H^{24}O^4,PH^3O^8 + 16aq.$ | 990 | ........ | 100·00 |  |  |

*Bihydriodate of Quinine*, $C^{40}N^2H^{24}O^4,2HI + 10HO$. — Obtained in fine prisms and laminæ, on mixing a slightly warmed acid quinine-solution with iodide of potassium. It gives off a considerable quantity of water between 30° and 40°, becoming opaque at the same time. Melts in its water of crystallisation when quickly heated to 100°, and gives off the whole of it, amounting to 13·51—13·92 (calc. for 10 at. = 13·40) at about 120°. The dehydrated salt gave by analysis 43·63 and 43·86 p. c. iodine, the formula $C^{40}N^2H^{24}O^4,2HI$ requiring 43·79 p. c. When exposed to moist air, it quickly recovers 4 at. water.

*Chlorate of Quinine*, $2C^{40}N^2H^{24}O^4,ClHO^6 + 7HO$. — Prepared by decomposing sulphate of quinine with chlorate of baryta, keeping the quinine-salt in slight excess, and afterwards removing the excess of sulphuric acid by digestion with carbonate of baryta. Crystallises in small mushroom-shaped masses, composed of filiform snow-white crystals. 1 pt. dissolves in in 78·5 pts. of cold water. Very soluble in boiling water, and in spirit. Febrifugal (F. C. Tichborne, *The Chemist and Druggist*, Sept., 1866, p. 137).

*Hydrochlorate of Quinine* (comp. p. 282), $C^{40}N^2H^{24}O^4,HCl + 4HO$. —

Long, asbestiform prisms, which do not effloresce in the air at ordinary temperatures, but easily give up their water of crystallisation at 120°. One part of the salt dissolves in 39·4 pts. water at 10°. Gives by analysis 8·93—9·05 water and 8·92 chlorine (calc. 8·95 water and 9·08 chlorine).

*Arseniate of Quinine*, $2C^{40}N^2H^{24}O^4,AsH^3O^8 + 16HO$. — Obtained by double decomposition with hydrochlorate of quinine and arseniate of potash. Long white prisms, sparingly soluble in cold, easily in boiling water. Gives off 15·43 p. c. water at 105° ($16HO = 15·42$ p. c.), and the salt dried at that temperature give by analysis 10·64 p. c. $AsO^5$ (calc. 10·59 p. c.).

*Oxalate of Quinine* (comp. p. 273). — a. *Neutral*, $2C^{40}N^2H^{24}O^4,C^4H^2O^8 + 12HO$. Long prisms resembling the sulphate, efflorescent and soluble in 1030 pts. water at 10°. The crystals, heated to 125°, give off 12·76 p. c. water (12 at. = 12·76).

b. *Acid.* $C^{40}N^2H^{24}O^4,C^4H^2O^8 + 2aq.$ Obtained by dissolving 1 at. of the neutral salt and 1 at. oxalic acid in water, and leaving the solution to evaporate. Small prisms moderately soluble in cold water, and exhibiting an acid reaction.

|  |  |  |  | Hesse. |
|---|---|---|---|---|
| $C^{40}N^2H^{24}O^4$ | 324 | ........ | 75·01 | |
| $C^4H^2O^8$ | 90 | ........ | 20·83 | 20·60 |
| 2 HO | 18 | ........ | 4·16 | 4·03 |
| $C^{40}N^2H^{24}O^4,C^4H^2O^8 + 2$ aq. | 432 | ........ | 100·00 | |

*Succinate of Quinine*, obtained by direct combination, forms long white prisms, which dissolve very easily in boiling water and alcohol, much less in the same liquids at ordinary temperatures. 1 pt. dissolves at 10° in 910 pts. water.

|  |  |  |  | Hesse. |
|---|---|---|---|---|
| $2C^{40}N^2H^{24}O^4$ | 648 | ........ | 71·21 | 70·67 |
| $C^8H^6O^8$ | 118 | ........ | 12·97 | |
| 16 HO | 144 | ........ | 15·82 | 15·67 to 15·86 |
| $2C^{40}N^2H^{24}O^4,C^8H^6O^8 + 16aq.$ | 910 | ........ | 100·00 | |

When recrystallised from strong alcohol, or from boiling water containing an equivalent quantity of succinic acid, it still retains the same composition and the same amount of water.

*Citrate of Quinine* (comp. p. 292). — a. *Bibasic.* Obtained either by saturating quinine with citric acid (p. 292), or by decomposing hydrochlorate of quinine with citrate of soda acidulated with citric acid. When recrystallised from warm water, it forms white, mostly small prisms, soluble in 930 pts. water at 12°.

|  |  |  |  | Hesse. |
|---|---|---|---|---|
| 2 $C^{40}N^2H^{24}O^4$ | 648 | ........ | 67·08 | 67·33 |
| $C^{12}H^8O^{14}$ | 192 | ........ | 29·88 | |
| 14 HO | 144 | ........ | 13·04 | 13·14 to 13·35 |
| $2C^{40}N^2H^{24}O^4,C^{12}H^8O^{14} + 14aq.$ | 984 | ........ | 100·00 | |

b. *Monobasic.* $C^{40}N^2H^{24}O^4,C^{12}H^8O^{14}$. A solution of the bibasic salt in boiling water, mixed with somewhat more than an equivalent quantity of citric acid, deposits this salt on cooling in small white

prisms, which dissolve with some difficulty in cold and in hot water, imparting an acid reaction. They contain no water of crystallisation.

*Benzoate of Quinine,* $C^{40}N^2H^{24}O^4, C^{14}H^6O^4$, obtained by direct combination of quinine and benzoic acid, forms small white anhydrous prisms, which dissolve in 373 pts. of water at 10°, and give by analysis 72·37 p. c. quinine (calc. 72·64 p. c.).

*Eugenate of Quinine,* $C^{40}N^2H^{24}O^4, C^{20}H^{12}O^4$, is obtained by dissolving quinine and oil of cloves together in boiling spirit, the liquid as it cools depositing the salt in fine long silky needles. It dissolves to a slight extent in boiling water, the undissolved portion melting to an oil, which solidifies in the crystalline form on cooling. The aqueous solution, as it cools, also deposits the greater part of the dissolved salt in small prisms. 1 pt. of it dissolves in 12 pts. of ether at 12°. It is distinguished from all other quinine-salts in not being decomposed by ammonia or by caustic potash, dissolving in the alkaline liquid to a certain amount at the boiling heat, and crystallising on cooling. At 100° it forms a fused yellow mass, and continually gives off eugenic acid, which, however, cannot be completely removed in this manner. The salt is anhydrous, and gives by analysis 66·20 p. c. quinine (calc. 66·39 p. c.).
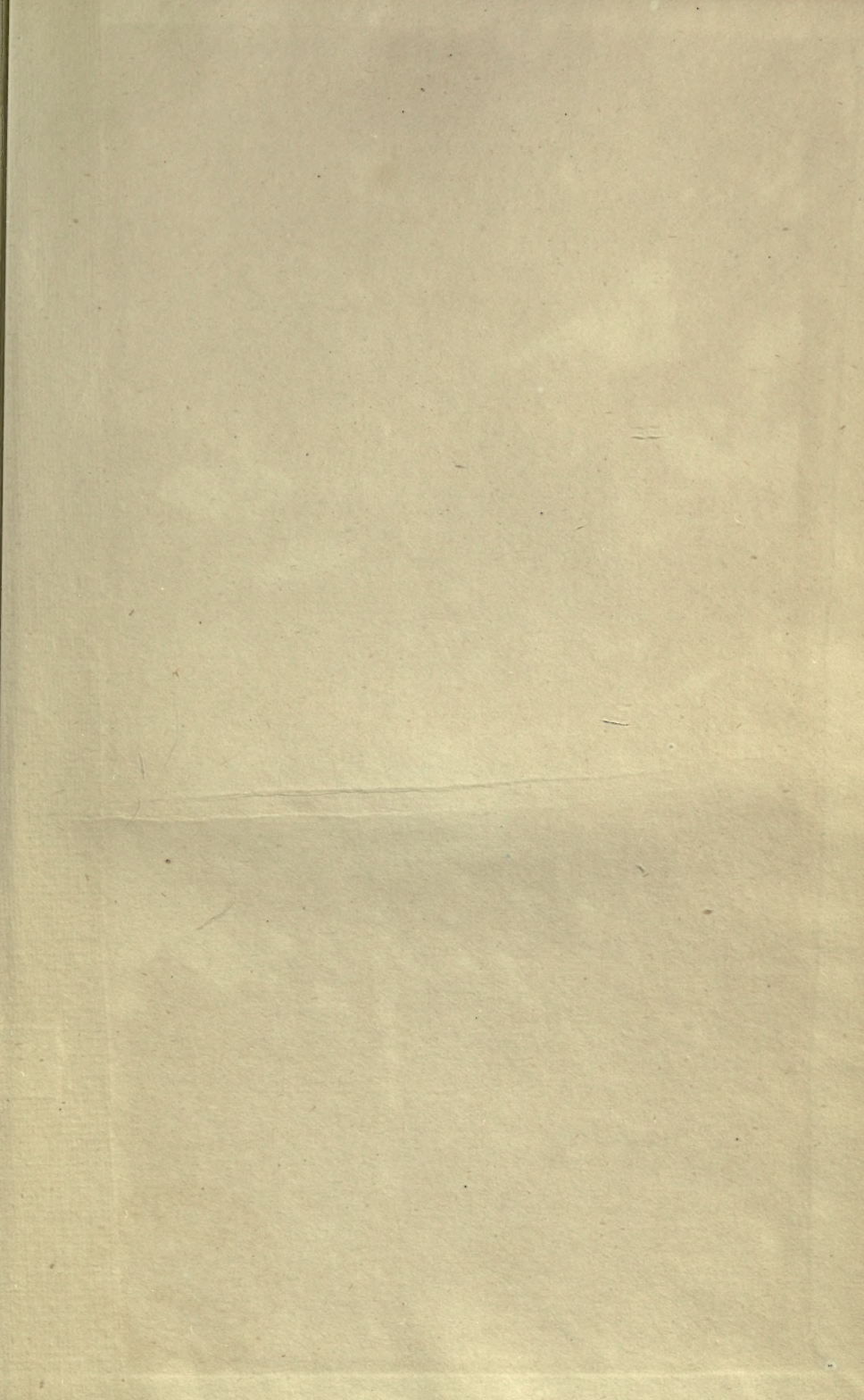
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## Resins.

The table on the next page gives the results of a recent investigation by Hlasiwetz and Barth (*Ann. Pharm.* cxxxiv, 265 ; *Bull. Soc. Chim.* 1866, i, 62).

The method adopted for examining the products of decomposition by potash was as follows : A quantity of the resin, not less than two pounds, is divided into 8 equal portions, and each portion gradually added to 3 times its weight of potash-hydrate fused in a silver basin with a small quantity of water. The resin then melts, and soon forms with the alkali a homogeneous mass, surmounted by a thick scum; aromatic vapours are evolved; and the resin is oxidised with evolution of a large quantity of hydrogen. The operation must be stopped as soon as this evolution of gas ceases, and the mass when cold, is treated with about 4 times its weight of water, and then with a sufficient quantity of sulphuric acid to render the solution acid. A certain quantity of resinous matter is thereby separated (oxidised resin analogous to copal) varying in bulk according to the nature of the original resin. The neutralised liquid, freed from resin and filtered, is shaken up with ether, the ethereal solution is evaporated to dryness, and the residue is taken up with water and precipitated by acetate of lead. This precipitate is washed, suspended in water, and decomposed by hydrosulphuric acid, and the liquid filtered and evaporated, finally yields a crystallised body.

| GUAIAC RESIN | DRAGON'S BLOOD | BENZOÏN | GALBANUM | ALOES |
|---|---|---|---|---|
| *contains:* | *contains:* | *contains:* | *contains:* | *contains:* |
| $C^{40}H^{26}O^4$ guaiacic acid. | $C^{40}H^{20}O^4$ (?) resin, soluble in ether, according to Johnston. | $C^{70}H^{34}O^{14}$ (?)<br>$C^{40}H^{14}O^8$—10 (?) $\Big\}$ resins.<br>$C^{30}H^{40}O^4$—10 (?)<br>$C^{46}H^{20}O^{12}$ benzo-cinnamic acid.<br>$C^{14}H^6O^4$ benzoic acid. | $C^{40}H^{26}O^6$ (?) resin.<br>$C^{20}H^{16}$ oil of galbanum (gum). | $C^{34}H^{16}O^4$ aloin.<br>$C^{30}H^{16}O^4$ alveretic acid. |
| *Yields by dry Distillation.* | *Yields by dry Distillation:* | *Yields by dry Distillation:* | *Yields by dry Distillation:* | *Yields by dry Distillation:* |
| $C^{38}H^{22}O^6$ pyroguaiacin.<br>$C^{16}H^{10}O^4$ creosol.<br>$C^{14}H^8O^4$ gaiol.<br>$C^{30}H^2O^2$ guaiacene. | $C^{16}H^8$ metastyrol.<br>$C^{14}H^8$ toluol.<br>$C^{14}H^6O^4$ benzoic acid. | $C^{14}H^6O^4$ benzoic acid.<br>$C^{12}H^6O^2$ phenylic alcohol. | $C^{90}H^3O^2$.<br>$C^{12}H^6O^4$ umbelliferone. | $C^{16}H^{12}O^6$ aloisol. |
| *Oxidised by Potash.* | *Oxidised by Potash:* | *Oxidised by Potash:* | *Oxidised by Potash:* | *Oxidised by Potash:* |
| $C^{18}H^{10}O^6$.<br>$C^{14}H^6O^8$ protocatechuic acid. | $C^{28}H^{14}O^{14}$ $\Big\{$ para-oxybenzoic acid. protocatechuic acid.<br>$C^{18}H^8O^{10}$ (?) the body which gives a red coloration with ferric chloride.<br>$C^{14}H^6O^4$ benzoic acid.<br>$C^{14}H^6O^6$ para-oxybenzoic acid.<br>$C^{14}H^6O^8$ protocatechuic acid.<br>$C^{12}H^6O^6$ phloroglucin. | $C^{28}H^{12}O^{14}$.<br>$C^{18}H^8O^{10}$ (?).<br>$C^{14}H^6O^4$ benzoic acid.<br>$C^{14}H^6O^6$ para-oxybenzoic acid.<br>$C^{14}H^6O^8$ protocatechuic acid.<br>$C^{12}H^6O^4$ oxyphenic acid. | $C^{22}H^9O^4$ resorcin. | $C^{14}H^8O^4$ orcin.<br>$C^{14}H^6O^6$ para-oxy-benzoic acid. |